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THE EFFECT OF MOISTURE ON THE PROPERTIES OF AN ARAMID/EPOXY COMPOSITE

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COMPOSITES DEVELOPMENT DIVISION

May 1983

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ABSTRACT

An investigation has been carried out concerning the effects of moisture on the mechanical properties of a unidirectionally reinforced Kevlar/epoxy composite. The matrix chosen was a so-called high performance exoxy - Fiberite 934. It consists primarily of tetraglycidyl-methylene dianaline (TGMDA) cured with diaminodiphenyl sulfone (DDS) at 177^oC (350^oF). The material was characterized by liquid chromatography, differential scanning calorimetry, torsional braid analysis, and Fourier transform infrared spectroscopy, in order to assure continuity with future work. The material was obtained from Fiberite in the form of B-staged prepreg tape. Seven-ply laminates were laid up from the prepreg by hand, vacuum bagged, and autoclave cured according to the recommended cure cycle. A very slow cooling rate was required to suppress the spontaneous axial cracking which occurs due to differences in thermal expansion coefficient of the fibers ($-2 \times 10^{-6}/^oC$ axially) and the epoxy ($50 \times 10^{-6}/^oC$). The moisture content of the laminates was varied by conditioning at 50^oC. The dry specimens were held in a vacuum oven for one to two weeks, depending on thickness. The wet specimens were immersed in distilled water for two to three weeks. The dry material has a glass transition temperature of 205^oC as determined by torsion pendulum measurements, while the wet material, at a moisture content of approximately 5% by weight, has a Tg of 150^oC.

Quasi-static mechanical properties of the composite were studied as a function of moisture content, as were the properties of Kevlar yarns and unreinforced 934 epoxy. Absorption of moisture was found to decrease the yield stress of the unreinforced resin measured in compression by almost 50%, and to increase strain to failure by approximately 15%. Although brittle fracture in the unreinforced resin masks this increase in deformability when measurements are performed in tension, it is manifested in the wet composite by higher strain to failure, higher irrecoverable strain, lower acoustic emission at low stresses, and approximately 10% higher ultimate strength. The higher strength may be due to a more uniform distribution of stresses in the wet material.

Although the wet composite has a 10% higher single-cycle strength, normalized S-N curves of wet and dry composites show that both materials lose 6-7% of ultimate tensile strength per decade of loading in tension-tension fatigue at 10 Hz. By comparison, the normalized strength loss of unimpregnated Kevlar yarns under these conditions is only 1-2% of ultimate tensile strength per decade. These results suggest that the mechanism of fatigue failure is the same in wet and dry composites, and is dominated by the presence of the matrix, since the composite behavior differs substantially from that of the dry fibers. Scanning electron micrographs of wet and dry fatigue specimens reflect the occurrence of fiber abrasion during fatigue loading. Other similarities, such as a 6-7% loss of fiber ultimate tensile strength per decade of abrasion cycles in yarns abraded under tension indicate that some form of fiber/matrix abrasion may be the mechanism of fatigue failure in these composites.

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ACKNOWLEDGEMENTS

This thesis is dedicated with love to my husband David, my children Stephen and Patricia, and all my family. Their help, and my gratitude and affection for them, are beyond description.

I. INTRODUCTION

In 1972, the E.I. DuPont Company introduced an aromatic
polyamide fiber which they first marketed as PRD-49 and is
now known by the trademark Kevlar. (1)* In the years since
then, this material has generated extensive interest and
also concern. Due to an extremely high degree of orienta-
tion of the polymer chains along the axis of the fiber, it
possesses remarkably high strength and stiffness in tension,
and although these properties have declined somewhat since
the material was first introduced, (the reported modulus has
decreased from 23 to 18 Mpsi) they are still by far the
highest of any commercially available organic fiber. Nor-
malized by the relatively low density to be expected in an
organic material (1.44 g/cc), Kevlar's specific tensile
strength and stiffness render it a compelling candidate for
any application requiring high strength and stiffness to
weight ratios - particularly in the field of aerospace, and
transportation generally.

The problems which deter many potential users from
availing themselves of these properties in current design
arise from the same factors (extreme anisotropy and organic
composition) which lend the material high specific axial
properties.

With such high axial orientation, essentially all of the

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* Numbers in parentheses refer to sources cited in the
Bibliography.

covalent main-chain bonds are along the fiber direction, leaving only the hydrogen bonds characteristic of a polyamide to hold the material together radially. Thus the transverse strength of the fiber is quite low, causing problems both in transverse strength of aramid/epoxy laminates (approximately 1 kpsi), and in compressive and flexural strength as well. As a result, most actual usage of these fibers has been in applications utilizing only tensile properties such as filament-wound pressure vessels for rocket motor cases and containment of gasses under pressure, or cables for lightweight applications such as highly portable assault bridges, or the man-powered aircraft Gossamer Albatross which was successfully flown across the English Channel in 1979 (2). (See Figure 1.)

In the last case, the success was due primarily to the magnificent performance of the human power plant, but without the carefully designed minimum weight structure, his efforts would have been in vain.

This kind of weight saving would clearly be beneficial for commercial aircraft, but in addition to the problems with off-axis properties, which could in theory be overcome by careful design, there is very limited data available on the behavior of these materials in fatigue. An understanding of this behavior is a prerequisite for utilization of any material in aircraft structures.

Also, since Kevlar is organic in nature, it is susceptable to moisture absorption, and in fact absorbs amounts of
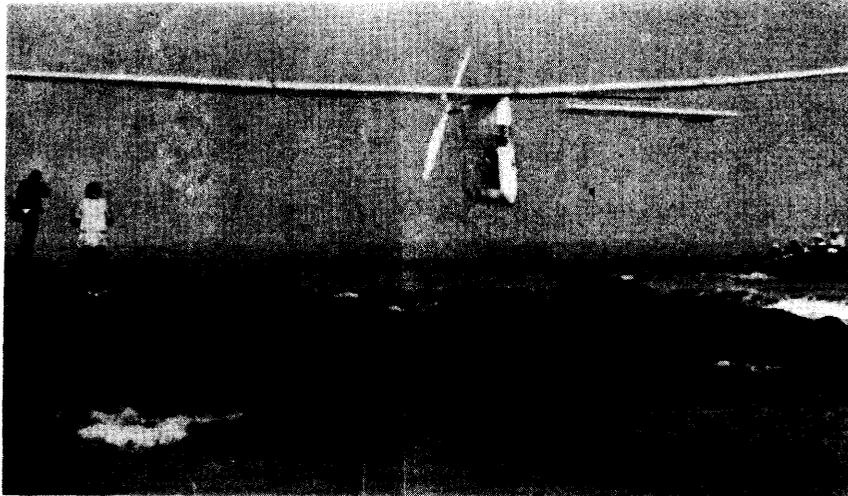
Figure 1 - The Gossamer Albatross (2).

atmospheric moisture comparable to that absorbed by many organic matrices. The effects of this absorption on the properties of the fibers and laminates fabricated from them are not well understood.

The use of Kevlar/epoxy composites in aerospace applications would require stability in the presence of environmental moisture. This study was therefore undertaken to examine the effect of moisture absorption on the mechanical properties of such a composite, including resistance to fatigue loading. The object was both to generate engineer-

ing data, and to develop an understanding of the basic processes which control the properties of the material. This requires a basic understanding of the nature of the constituent fiber and matrix.

A significant part of this study was devoted to a thorough characterization of the chemical composition and curing behavior of the specific epoxy chosen, since variations in resin composition or processing can result in variations in composite properties, particularly with regard to interactions with moisture. Also, this work is part of an ongoing effort, and if correlations are to be made between these data and those obtained in the future, the materials must be essentially the same throughout the study. Commercial suppliers of composite materials have been notorious in the past for changing formulations and prepregging techniques without notification of customers, and careful characterization is essential to avoid unpleasant surprises.

II. MATERIALS

A. <u>Kevlar</u> <u>Aramid</u> <u>Fibers</u>.

The aromatic polyamide ("aramid") fibers used in this study were obtained from the E. I. DuPont Co. directly for the fiber testing and through Fiberite, Inc. in the form of a tape preimpregnated with partially cured epoxy resin - the so-called "prepreg." The fiber is sold as Kevlar 49, a high-modulus type intended for structural applications.

The development of Kevlar at DuPont is an interesting example of a cooperative industrial effort. The pioneering synthesis work was performed by a team led by Dr. Paul Morgan. Ms. S. Kwolek discovered that sufficiently high concentrations of the polymer in the proper solvents formed anisotropic spinning dopes, or nematic liquid crystals, due to the rod-like structure of the molecules in solution. This lead to the development by Dr. Herbert Blades of the so-called dry-jet wet spinning process which produces very highly oriented fibers without subsequent deformation processing, although a high-temperature (550-600°C) annealing under tension is apparently required to maximize stiffness.

In 1976 Dr. Morgan was presented by the American Chemical Society with the Witco prize, and to commemorate the occasion a number of excellent papers concerning this development were published (in the ACS Polymer Preprints) by various workers from DuPont (3-8).

The exceptionally high axial strength and stiffness of

this fiber are as mentioned, due to the high degree of axial molecular orientation which it possesses. In X-ray crystallographic studies (9), Kevlar 49 was observed to have a chain direction orientation function of $f(c) = 0.964$, which corresponds to a x factor of $5^\circ - 5.5^\circ$. This is the angular range in which the diffracted X-ray intensity drops from maximum to half-maximum.

The chemical, crystallographic and supramolecular structure of Kevlar 49 have been indentified in a number of studies (9-14) using techniques which include nuclear magnetic resonance, electron microscopy and electron diffraction. It has been shown to be poly(paraphenylene terephthalamide), the structure of which is:
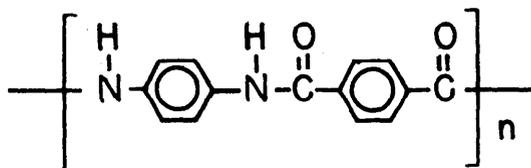
This polymer is formed by the condensation of p-phenylene diamine with terephthalic acid chloride. Details of its synthesis are proprietary to DuPont, but some information is available on the polymerization of this and other aromatic polyamides (3-8,15,16). They are thought to be prepared by the addition of the diacid chloride to a cool $(5-10^\circ C)$ agitated solution of the diamine. The solvent system currently is not known outside DuPont, but before 1976 DuPont was

using hexamethyl phosphoramide (HMPA) which was discontinued after questions arose concerning its safety.

Although the molecular weight of this material is very difficult to determine due to the liquid crystal nature of the polymer in solution (17), the resultant polymerization product is low in molecular weight, even for a condensation polymer. For spinning, the polymer is probably redissolved in sulfuric acid, and spun by the dry-jet wet spinning process described by Blades (18). After spinning, the fiber is treated with sodium hydroxide to neutralize the residual sulfuric acid. Chemical analysis of the fibers shows the presence of sodium sulfate in the fibers as a result of this treatment, and the sulfate content is reported in some cases (19) to vary considerably from batch to batch. Since the sodium sulfate absorbs moisture, there is a corresponding variation in the equilibrium moisture content of the fibers from batch to batch. Other investigators (20) have not reported such severe variations. To avoid these problems, all laminates tested in the present study were fabricated from a single batch of prepreg material, which was in turn fabricated from a single fiber batch.

The fiber morphology which results from this process is fairly complex. The molecules in solution are in a highly extended configuration and as the fiber is formed they apparently are deposited almost exclusively in the direction of the fiber axis. The fiber is very highly crystalline, and the unit cell is monoclinic (pseudo-orthorhombic) with

dimensions:

$$a - 7.78 - 7.87A$$
$$b - 5.18 - 5.28A$$
$$c - 12.9A \quad \text{(fiber axis)}$$
$$\gamma - 90°$$

The supramolecular structure of Kevlar has been studied
(13,14) using chemical degradation, X-ray and electron dif-
fraction, and electron microscopy. The highly extended
polymer chains apparently pass through defect zones which
occur every 200-300A while maintaining crystallographic reg-
ister in the adjacent lamellae. Alternating disordered and
ordered lamellae are arranged in columns 5000-7000A in diam-
eter which constitute the fibrils which are characteristic
of Kevlar microstructure. The fibrils are bonded together
in radially-arranged layers or sheets which undergo a slight
change in orientation (or "pleats") every 2000-3000A. Dobbs
et al. (13) estimate that these sheets are oriented at 170
to each other. They note that in the highest modulus vari-
ety of this fiber, PRD-49, this pleated sheet organization
is absent. Many investigators (21,22) have produced micro-
graphs which indicate that the very low transverse strength
of the fiber is due to the breakdown under load into these
microfibrils (see Figure 2), although these splits can often
extend much further along the fiber in fatigue than in sim-
ple tensile loading, the fiber fracture modes in tension and
tension-tension fatigue are similar. On the basis of

- 19 -
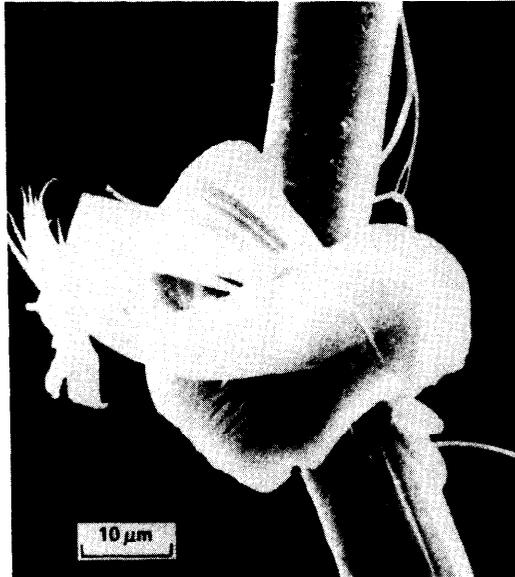
Figure 2 - Kevlar filament splitting at knot (45).

observations of failure modes, and measurements of acoustic emission during fiber failure, Bunsell (22) estimates that perhaps three quarters of the strain energy in a simple tensile test going to creating fracture surface and nonrecoverable plastic deformation.   This may contribute to the relatively high toughness of Kevlar composites, and to its usefulness in high rate projectile impact protection.   The use of Kevlar in bullet-impact protective clothing and other related applications is one of its most important applications.   This fibrillar morphology may also give rise to

abrasion sensitivity in some cases.

An excellent general review of the structure and proper-
ties of Kevlar fiber and Kevlar/epoxy composites is to be
found in a chapter of the forthcoming "Handbook on Fiber-
glass and Plastic Composites," written by C.C. and T.T.
Chiao of Lawrence Livermore Laboratories (23).

B. Fiberite 934 Epoxy Resin.

Fiberite 934 is a 350°F (177°C) cure epoxy resin prod-
uced by Fiberite Corp. of Winona, Minnesota. For this study
it was obtained both as uncured liquid resin and as
B-staged, or partially cured, resin in the Kevlar prepreg
tape. The tape obtained was fabricated in a single batch
using the same resin batch from which the uncured resin was
supplied.

Although each manufacturer adds slightly different mate-
rials in small amounts, Fiberite 934, Narmco 5208, Hercules
3501 and a number of other 350°F cure resins all employ the
same epoxy: tetraglycidyl methylene dianaline (TGMDA) and

TGMDA:
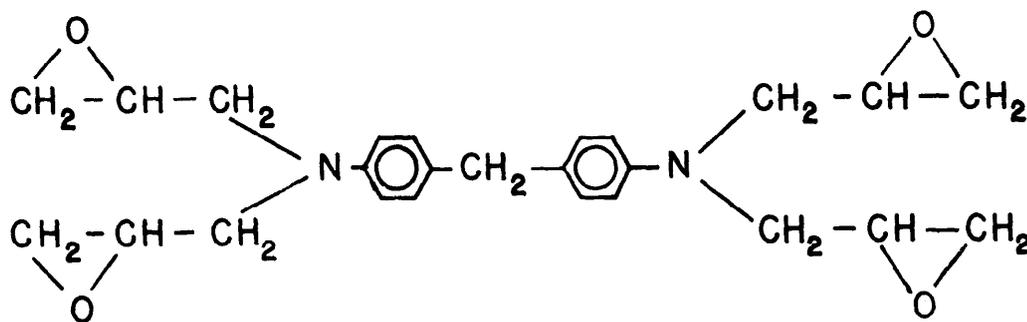
the same curing agent: diamino diphenyl sulfone (DDS).

DDS:

$$H_2N-\bigcirc-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}-\bigcirc-NH_2$$
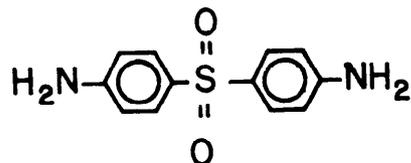
In the case of Fiberite 934, the manufacturer adds a boron trifluoride - monoethyl amine complex as a catalyst. Chemical analysis indicates that the Fiberite 934 composition is roughly:

TGMDA	60-65% by volume
DDS	25-30%
BF3-MEA	0.3-0.5%

The remainder of approximately 10% by volume is probably a diglycidyl ester of orthophthalic acid, probably added to improve handling characteristics of the prepreg (24).

A general review of the physical and mechanical properties of this epoxy has been published by Morgan and O'Neal (25). There is considerable evidence for an inhomogeneous microstructure in this material which may be due in part to the imperfect solubility of the DDS, a crystalline solid

with a melting point of 162°C, in the TGMDA, which is a vis-
cous liquid at room temperature. We have found evidence for
the presence of crystalline DDS in the curing resin at ele-
vated temperatures, and the observation of regions of high
concentrations of sulfur in fracture surfaces of this mate-
rial by X-ray emission scanning spectroscopy indicate that
the unreacted DDS may persist in the cured resin (see Figure

100 μm

Figure 3 - Sulfur distribution in the fracture surface
of TGMDA/DDS epoxy (25).

3). Other less conclusive evidence suggests the presence of
regions of highly crosslinked material embedded in a contin-

uum of lower crosslink density.

Whatever its morphology, this material (25) is strongly plasticized by absorbed moisture as evidenced by a drop in the glass transition temperature from near 200°C to near 150 C in the saturated material. A decrease is observed in the strength and stiffness of the wet resin in tensile tests, and the decrease becomes more prominent at elevated temperatures. There is also a decrease of approximately 5% in what Morgan and O'Neal call the microyield stress, that is the stress at the onset of nonlinear behavior in the tensile stress-strain curve. They state that this yield stress is closely associated with the onset of localized flow and cavitation. They also present scanning electron micrographs of extensive cavitation and deformation in room temperature fracture surfaces in the wet material.

A discussion of the curing behavior of this resin is to be found in the section on characterization below.

III. CHARACTERIZATION AND FABRICATION

A. Characterization of Resin.

The chemical characterization techniques employed in this study were essentially the same for neat resin and prepreg resin samples. These techniques included liquid chromatography (LC), differential scanning calorimetry (DSC), and torsional braid analysis (TBA). The primary objectives of the characterization of resins were 1) determination of chemical composition of neat and B-staged resins and 2) study of the curing behavior of these resins.

1. Liquid Chromatography.

Liquid chromatography is a primary method of chemical characterization for quality control, since with proper choice of a solvent system and detector a reproducible and easily recognizable "fingerprint" can be obtained. Each important component of the resin produces a separate peak whose magnitude reflects the quantity of that specimen fraction.

For the 934 resin and Kevlar/934 prepreg, the technique developed was one used earlier for characterization of aging of Hercules 3501/AS graphite/epoxy prepreg (26). A Waters Associates high pressure liquid chromatograph ALC/GPC-244 was used with a solvent system which employed a linear gradient from 50%-50% isooctane with tetrahydrofuran (THF) to 100% THF over twenty minutes at a flow rate of 2.0 ml/min.

The effluents were monitored using 254 and 280 nm ultra-
violet detectors, although the 280 nm detector gave a much·
superior baseline.

In Figure 4, the LC fingerprints for 934 resin from two
shipments illustrate the ability of this technique to dis-
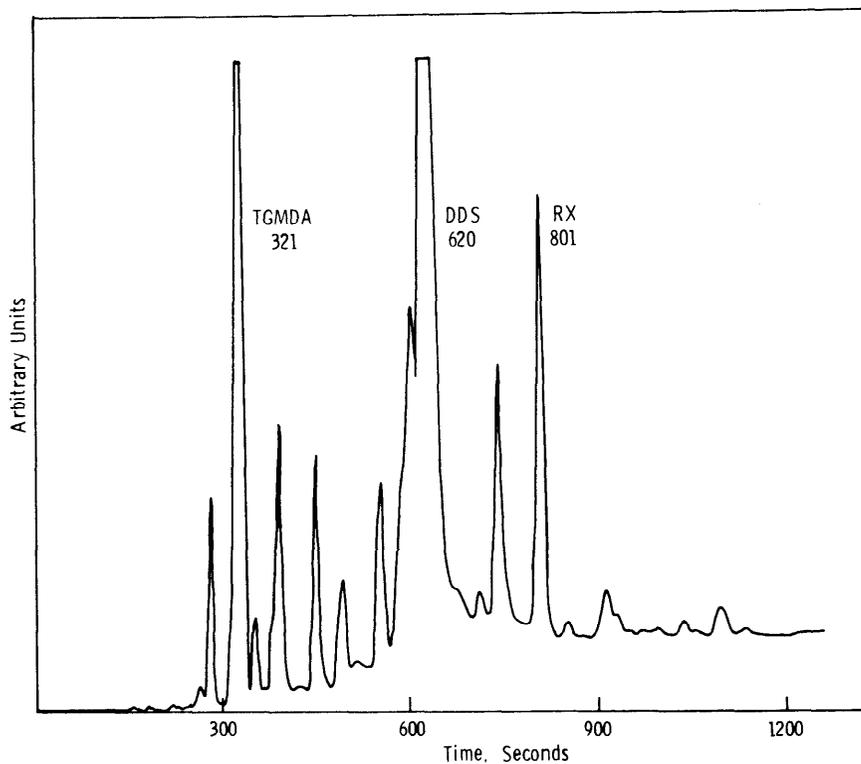
Figure 4a - Liquid chromatography (LC) fingerprint
of Kevlar/934 prepreg.

tinguish differences in extent of cure. The peaks at 321,
620, and 801 seconds reflect the TGMDA, DDS, and a reaction
product of the two, respectively. The volume percent of
this reaction product (which is most probably TGMDA-DDS-
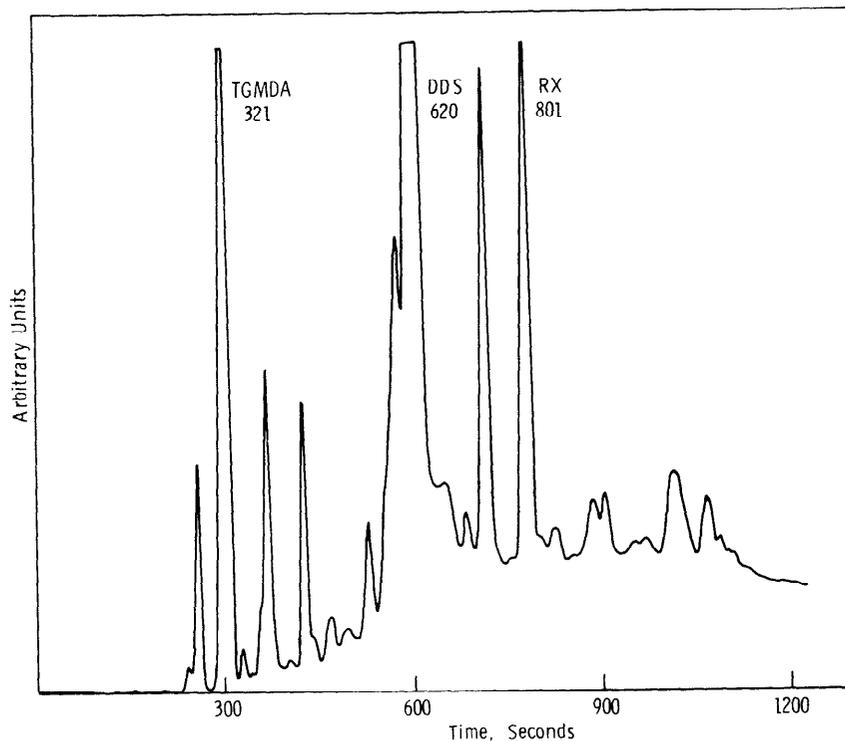
Figure 4b - LC fingerprint of improperly shipped prepreg.

TGMDA) is calculated to be 3.78% in the first shipment and 2.84% in the second. This first shipment was made by truck and the dry ice in which it was shipped lasted only some 48 hours of the weeklong shipping time. The second smaller shipment was made by air. Since there are apparent differences in these two shipments of resin, all resin testing was performed on material cast only from the first batch.

Prepreg aging can have a significant effect on moisture uptake and mechanical properties of the cured laminate. It is proposed to study this effect as an extension of the

present work, and LC - along with TBA - will be an important tool in this study. One important step in LC prepreg studies is the dissolving of the B-staged resin in the selected solvent, and we have found that Kevlar fibers have a much stronger affinity for various components of this epoxy than do graphite fibers. Care must be taken to dissolve the resin completely, especially the higher molecular weight components.

2. Differential Scanning Calorimetry.

DSC was used to observe the magnitude and nature of the curing exotherm in the neat resin and in the prepreg. A Perkin-Elmer DSC-II was used for all measurements, with temperature scanned at $20^{\circ}C/min$ from $27-287^{\circ}C$ $(300-560^{\circ}K)$. The same specimen pans were used for resin and prepreg, with the prepreg specimen consisting of two layers of material containing approximately 40 wt% of B-staged resin. The DSC thermogram for the prepreg material is shown in Figure 5. Integration of the area under the exotherm yields a value of 70 cal/gram (290 J/gram). This exotherm is apparently composed of two or three separate processes.

The onset of cure occurs at approximately $106^{\circ}C$, which is the temperature at which the BF3-MEA complex becomes active. The increase in reaction rate at $158^{\circ}C$ seems to correspond to the melting point of the crystalline DDS at $162^{\circ}C$, and indicates that a significant amount of the DDS present is not dissolved in the liquid epoxy. This
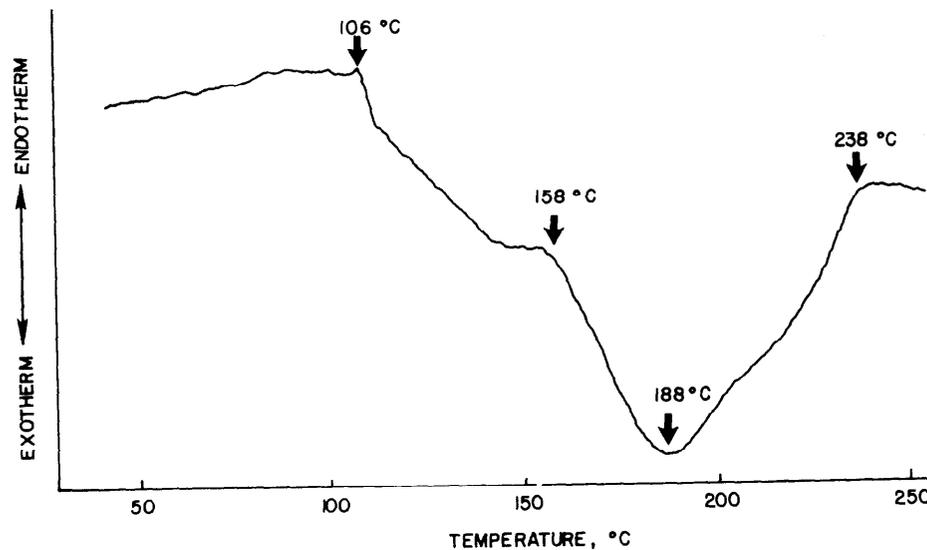
Figure 5 - DSC thermogram for Kevlar/934 prepreg.

crystalline DDS has been reported by Morgan (25) to persist
even in the cured epoxy. The maximum in the exotherm lies
at 188°C, 10-15°C higher than the cure temperature recom-
mended for this prepreg.

The recommended cure cycle for the laminate also
involves a hold of one hour at 122 C°(250°F), with pressure
applied sometime during the hour. The time of application
of the pressure is important, since the material will not be
properly compacted if the viscosity of the resin is either
too high or too low. This would correspond to too much or

too little advance of the cure. It is clear from the DSC results that the curing reaction is proceeding at 122°C, a conclusion corroborated by the TBA data to be discussed below. On the basis of these data, we decided to apply pressure fairly early in the hold at 122°C, after 15 minutes.

3. Torsional Braid Analysis.

Another technique developed to study curing kinetics and aging of epoxies is torsional braid analysis (TBA). This technique has been used with some success to study aging of TGMDA/DDS epoxy both alone and in graphite prepreg. We have worked with Prof. J.K. Gillham to develop suitable techniques and equipment for handling prepreg braids. In place of the usual braid - a fine braid of glass fibers coated with polymer from solution - a thin strip of the actual prepreg is fitted with holders at the ends and inserted into the temperature chamber.

The measurement consists of a torsional displacement at the top of the braid and the monitoring of the resulting damped oscillations by means of a transducer disk attached to the bottom of the braid. Prof. Gillham's most recent development of the torsional braid analyzer automatically reactuates when oscillations from the previous actuation have dropped below a certain preset value, and also automatically prints and plots the logarithmic decrement (logarithm of the ratio of successive amplitude maxima) and the inverse

squared period (which is proportional to the shear modulus of the specimen-braid composite). The decrement is a measure of the energy dissipated per cycle of loading.

As shown in Figure 6, this measurement is very sensitive to the curing process. Figure 6 is a temperature scan at
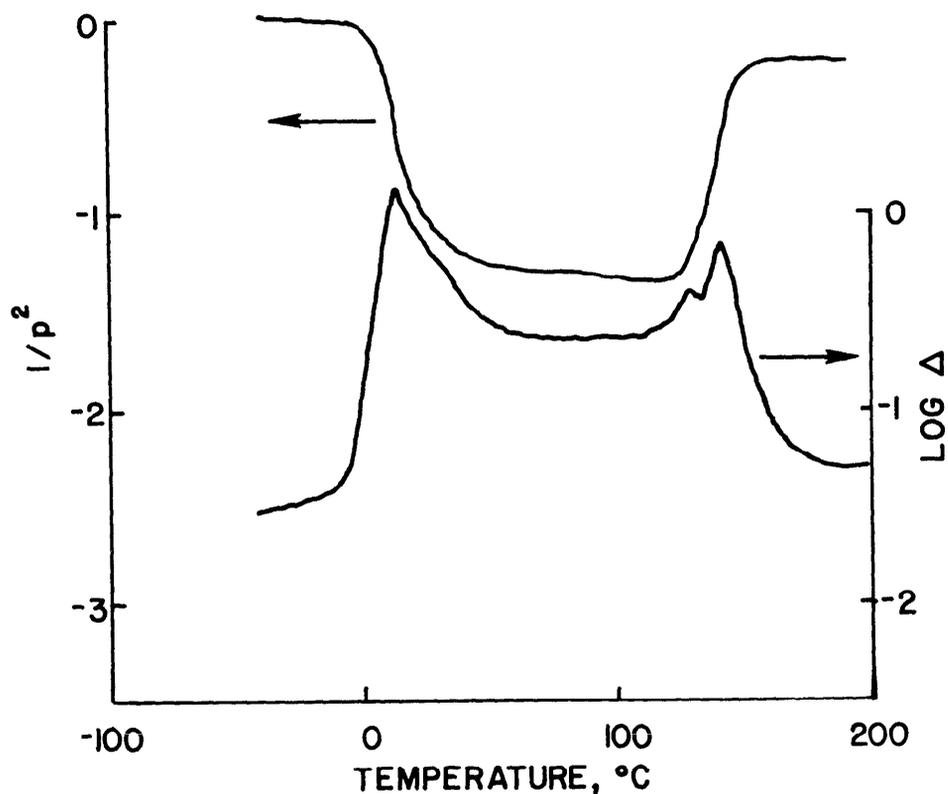
Figure 6 - Torsional braid analysis of
the curing behavior of Kevlar/934 prepreg.

0.15°C/min of a Kevlar/934 prepreg braid. Initially in its B-staged state the glass transition temperature of the resin is approximately 13°C, indicated by the drop in the modulus of one to two orders of magnitude, and the corresponding

peak in the decrement.   The glass transition temperature of the B-staged resin is very sensitive to prepreg aging, and its increase to some temperature above room temperature results in a so-called "boardy" prepreg, one which may no longer be processed.

The viscosity of the resin, reflected in the shear modulus curve, continues to decline until approximately $100^{o}C$, at which point cure of the resin begins (as also indicated by DSC) and the modulus begins a rapid increase. What Gillham has termed the gelation peak, corresponding to a region of rapidly increasing viscosity, occurs at $129^{o}C$, and high temperature vitrification of the curing resin occurs at $140.5^{o}C$ in this measurement.

In other words, at 140.5 C the glass transition temperature of the curing resin is increasing more rapidly than the scan temperature and has passed beyond it.   The ultimate glass transition temperature of the fully cured resin is approximately $205^{o}C$, and would be observed as another drop in modulus if the temperature were increased above $205^{o}C$. Glass transition temperatures of the cured materials were not measured as part of this curing study, but such measurements were performed using the torsion pendulum apparatus (TPA) and are discussed in detail in section IV on moisture effects.

These data are additional proof that the resin is curing quite rapidly at $122^{o}C$, leading us to apply pressure after fifteen minutes at $122^{o}C$ during the autoclave cure. This is

discussed in the next section on laminate fabrication.

B. Fabrication of Laminates.

The laminates used in this study were fabricated by hand layup from a single batch of "hy-E 1734A" prepreg received in a single air shipment from Fiberite, Inc. This prepreg was prepared by them using 4560 denier Kevlar 49 type 968 fibers obtained from DuPont. It contained 40 wt% of resin solids. As discussed in section III.A., these materials were thoroughly characterized by various techniques to insure that material obtained for future work will be the same as the material used in this study. The material is supplied as a unidirectionally reinforced tape one ft. wide and this batch consisted of four rolls 350 ft. long. Three rolls have been used to produce laminates for the present study and one roll is reserved for a study of the effects of prepreg aging on laminate properties.

The prepreg was layed up by hand into 2'x4' 7-ply laminates. Iron constantan thermocouples inserted between plies 3 and 4 were used to monitor the temperature during cure, and aluminum-coated Kapton polyimide film electrodes 2"x2" were placed on the top and bottom surface for dc resistivity measurements. Teflon sheets were then placed on top and bottom of each laminate, the laminate was inserted between two 2.5'x4.5' steel caul plates and the entire assemblage was vacuum bagged in preparation for autoclave cure.

The Teflon film was used to facilitate removal of the

cured laminate from the caul plates and subsequent handling. Since the unidirectional Kevlar/epoxy laminate has a very low transverse strength (approximately 1 kpsi) and these 7-ply laminates are quite thin (35-42 mils), very careful handling was required to prevent axial cracking of the cured laminate.

Although use of the Teflon film eliminated cracking during handling, the laminate tended to develop spontaneous axial cracking in the interior of the laminate. Acoustic emission measurements indicate that this occurs during cooldown. To try to minimize this damage, the cooling rate used for the laminates in this study was very slow: 1-2°C/min. With this exception the cure cycle recommended by Fiberite was used for the laminates: 1) apply a vacuum to the laminate, 2) heat to 122°C (250°F) and hold for one hour, 3) apply 100 psi pressure after 15-30 minutes at 122°C, 4) heat to 177°C (350°F) and hold for two hours, 5) cool slowly to below 100°C, and 6) remove pressure and vacuum.

The DC resistivity measurements, sometimes called "iongraphing", were made to follow the cure of the laminate in the autoclave. A diagram of the equipment is shown in Figure 7. Figure 8 shows the laminate temperature as measured by the thermocouple and the voltage drop across the laminate as a function of time.

This voltage drop is inversely proportional to resin viscosity, since as the viscosity decreases the resin becomes a better conductor, probably due to diffusion of

AUTOCLAVE

STRIP CHART
RECORDER

10 Volt
Battery

Laminate

Electrodes

0 Volts   10 Volts
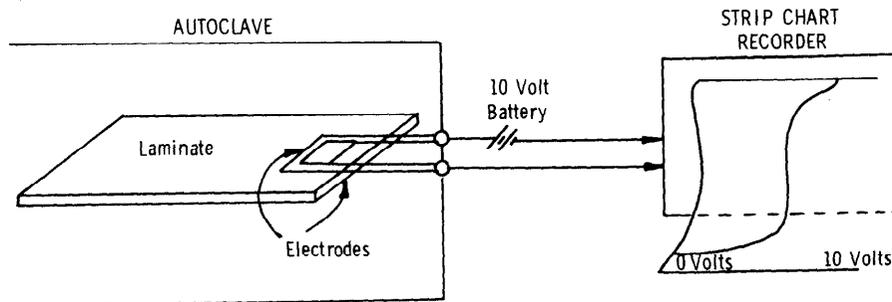
Figure 7 - Schematic of ion graphing apparatus.

ionic impurities. As the temperature is increased above room temperature the viscosity drops quite rapidly and remains fairly low throughout the hold at 122°C. As the temperature is increased from 122°C, the viscosity drops and then abruptly begins to increase at about 150°C, corresponding to the vitrification peak at 140.5°C observed in the TBA measurements at a much lower heating rate.

The cured laminates were removed from the vacuum bags and caul plates and stored in an air-conditioned room to await machining. Three inches of scrap was removed from around the edges of each laminate, and the remainder was cut into strips 0.5" wide by 8.5" long using a water cooled diamond wheel. This method is less than ideal for Kevlar composites, and leaves a very fuzzy surface which was cleaned with a sanding wheel. Laser cutting is the method recom-
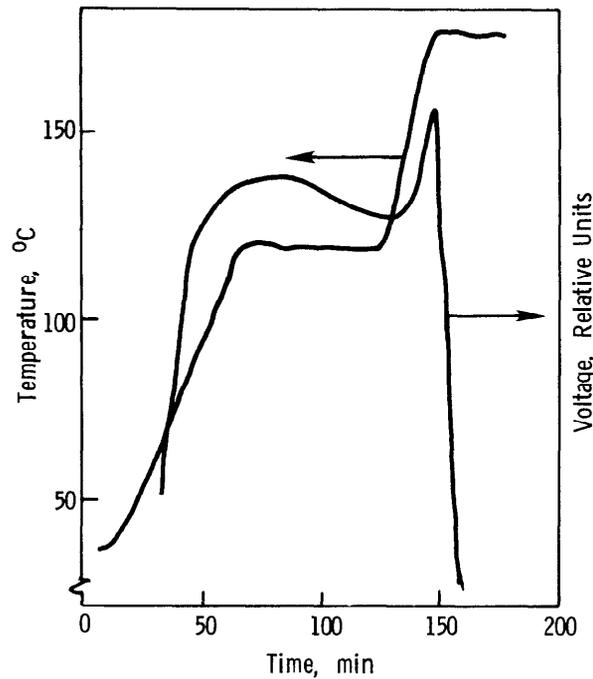
Figure 8 – Temperature and ion graphing curves for
Kevlar/934 laminate during cure.

mended most highly for Kevlar composites, although water-jet
cutting may be another attractive possibility.

C. Characterization of Cured Laminates.

The extent of cure of the laminates was studied using
fast Fourier infrared spectroscopy (FTIR). This technique
was also employed with cast plaques of pure 934 resin.

The FTIR spectrum of the uncured 934 resin is shown in
Figure 9, and this spectrum is shown as curve a in Figure 10

from 990-877 wavenumbers, the region of absorptions due to
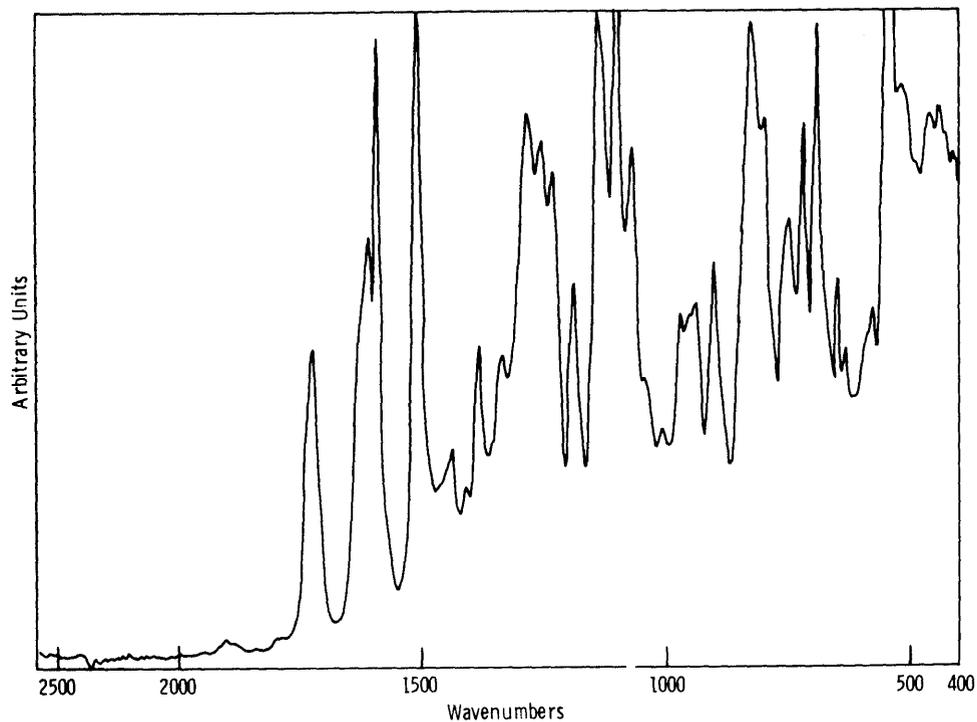
Figure 9 - FTIR spectrum of uncured 934 resin.

the epoxide bond. The technique usually used to measure degree of cure is to normalize the spectra on the basis of the aromatic 1510 wavenumber band in the uncured epoxy and then integrate the area under the curve from 990-877 waven-
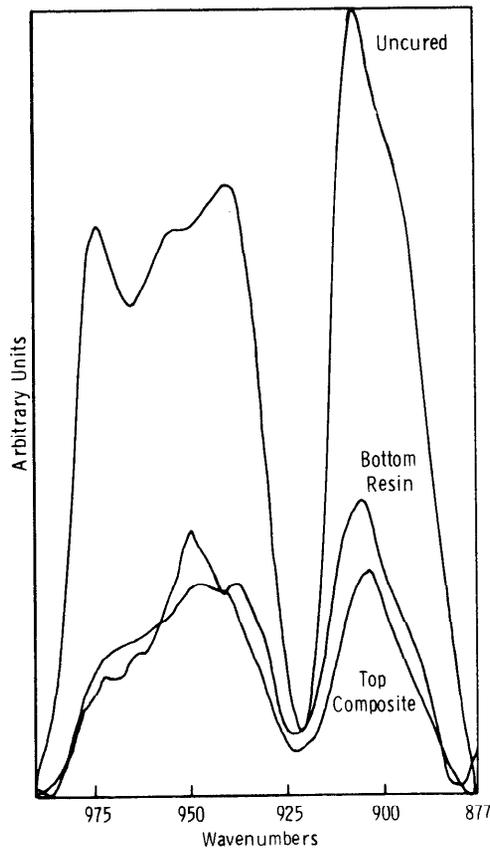
Figure 10 - FTIR spectra for uncured 934 resin,

cured 934 resin, and cured Kevlar/934 composite.

umbers. The ratio

$$R = \int_{990}^{877} A(F) \; dF \; \text{cured} \; / \int_{990}^{877} A(F) \; dF \; \text{uncured}$$

is then calculated for specimens of cured resin.

Figure 10 shows the spectra for a)   uncured epoxy, b)

cured epoxy, and c) cured laminate in the region from

990-877 wavenumbers. A problem arises due to an interfering

band between 918 and 877 wavenumbers.   This is not an epox-
ide band,   and may be due to the   presence of the Kevlar
fibers.   As a result the integration to determine extent of
cure has been performed from 990-918 wavenumbers.   The
results of these integrations are:

SPECIMEN	R
Uncured Resin	1.00
Cured Resin	0.27
Cured Laminate	0.26

The 25-30% unreacted epoxide, which occurs in both the
pure resin and the composite is to be expected from the
stoichiometric considerations illustrated in Table I from
reference 25.

Table I

THEORETICAL REACTION MIXTURES

FOR THE TGMDA-DDS EPOXY SYSTEM

	100% TGMDA	50% TGMDA
100% DDS prim&sec	37 wt% DDS	23 wt% DDS
100% DDS prim	54 wt% DDS	37 wt% DDS

Table I shows the weight percent DDS required, assuming
all the primary and secondary amines react, to consume 100%
or 50% of the epoxide groups in the tetrafunctional TGMDA
molecules. Steric restrictions present in the TGMDA make it
unlikely that many secondary amines react in this system.

As was discussed in section II-B, this 934 formulation con-
tains 25-35 wt% of DDS and 60-65 wt% of TGMDA. Even if all
the primary and secondary amines react, which is unlikely,
this concentration of DDS is insufficient to react with all
available epoxide groups.

Another possible cause for the presence of unreacted
epoxide is that the cure temperature is relatively low com-
pared to the glass transition temperature. They are 177 and
2°5 C respectively. The later stages of the cure are there-
fore carried out in a glassy matrix with a correspondingly
low diffusion rate. Torsional pendulum measurements which
we have performed after postcure show no increase in glass
transition temperature of the composite, but the glass
transition may not be sensitive to extent of epoxide conver-
sion in this range. Postcure and subsequent FTIR measure-
ments could distinguish the relative contribution of the two
potential causes of undercure. These measurements are sug-
gested as part of future work in characterization of this
material.

The measured value of 26-27% unreacted epoxide is a rea-
sonable one, in view of these considerations. Apparently
there is no difference in the degree of cure of the pure
resin and the resin in the composite, so in that regard
interactions with moisture should be similar. The resin in
the composite is not necessarily morphologically the same as
the pure resin, however. There may be some size effect due
to the fact that the matrix, although continuous, is

generally present as a thin layer between two adjacent fibers in the composite.

This leads to another important measurement in these composites: fiber volume fraction. An organic fiber/epoxy composite presents a unique problem since the fiber and matrix are both chemically and optically similar. These similarities lead to difficulties in the two standard techniques for measuring fiber weight or volume percent, which are 1) burnout or acid digestion of the matrix, and 2) quantitative optical microscopy. In conjunction with accurate measurement of composite density, burnout measurements can be used to determine the volume percent of fiber, matrix and voids. Quantitative optical microscopy can also provide spatial distributions of these volume fractions.

Although the Kevlar is considerably more thermally stable than most epoxies, it obviously cannot withstand burnout temperatures. It is also fairly impervious to most solvents, but anything which will dissolve a cured epoxy will eventually degrade the fibers somewhat. The most desirable technique for fiber volume measurement is quantitative optical microscopy, since it gives not only a fiber volume but also fiber spatial distribution. The optical density of the Kevlar fibers is very similar to that of the epoxy matrix, and although the fiber/matrix interface is usually fairly well defined (see Figure 34a), this is not sufficient for an area fraction measurement by means of automatic image analyzing microscopy, especially when there is some fiber-fiber

contact.

The best technique available is a sort of compromise.
It involves acid digestion of the composite with nitric acid
for a sufficiently long time to dissolve the epoxy, but not
long enough to attack the Kevlar. The technique is based on
one recommended for graphite/epoxy prepregs by J. Heth of
Fiberite, and the details are as follows:

1) Weigh composite specimen of 0.5-1.5 g.

2) Boil gently for one hour or "as required"
with 50 ml of 70% nitric acid in a 250 ml
Ehrlinmeyer flask with a condenser.

3) Cool, agitate to break up fiber bundles
and add 150 ml of distilled water.

4) Transfer to a fritted crucible, filter and
wash twice with 100 ml of acetone.

5) Dry at 325°F for 30 min.

6) Weigh fibers.

The crucial point here is in step 2 - one hour is far too
long for Kevlar/934 although it is standard for gra-
phite/934. The "as required" means when the fiber no longer
clumps when agitated but still retains its original color.
By trial and error we have found that 20 minutes is a suita-
ble time for laminates of this thickness. At this time,
microscopic observation of the fibers indicates that they
are clean and not damaged, although they do discolor
slightly after washing. This optimum time will vary with
laminate thickness, and should be carefully determined

before the technique is employed for a laminate thicker than that used here. In the case of thick laminates, this method may not be applicable since times required to dissolve all the resin may cause severe degradation of the fibers from the outer plies. Recent work (20) has indicated that pre-treatment of the Kevlar laminate with dimethyl sulfoxide (DMSO) may hasten the selective penetration of the nitric acid into the matrix, and thereby increase the thickness of laminates which can be characterized using this technique.

The fiber volume measurements indicated an inverse relationship between thickness and fiber volume. The range of laminate thickness of 0.035-0.042" corresponds to a range of fiber volume fraction from 70-64%. All tensile and fatigue strength data were normalized to 70% fiber volume fraction in this study. Void volume fractions were found to be less than 0.5% in all laminates.

IV. MOISTURE ABSORPTION.

A. Conditioning - Moisture Uptake.

All other variables have been held constant in so far as possible in this study in order to observe the effects of differing moisture content on the properties of the Kevlar/934 composites. This difference in moisture content has been achieved by two different conditioning histories, which are referred to here as "wet" and "dry" conditioning. The materials termed "dry" were held in a vacuum oven at $50^{\circ}C$ for one to two weeks, and those termed "wet" were immersed in distilled water at $50^{\circ}C$ for two to three weeks.

The 50 C temperature was chosen to hasten the approach to equilibrium, but is low enough to avoid failures which have been observed in this epoxy during higher temperature immersion due to surface swelling (20). The $50^{\circ}C$ is probably a conservative choice, and for future work, especially with thicker laminates or resin castings, a higher temperature (perhaps $75-80^{\circ}C$) should be used.

The conditioning time for the dry specimens was chosen by observing weight loss which slowed greatly after one week, and by monitoring the tensile strength of the material after conditioning. This showed changes up to approximately one week of drying and none thereafter. The problem of determining actual moisture content of these dry specimens was never completely solved, because adequate techniques for this measurement do not exist.

The most common measurement of moisture content is made by weighing the specimen, drying it at some elevated temperature, and then weighing it again. This method requires that the material exhibit a well defined plateau in weight loss versus temperature below the onset of thermal degradation. This insures that the measured weight loss is due only to drying, and not chemical or physical changes in the material. These Kevlar/epoxy laminates do not exhibit such a plateau.

B. Thermogravimetric Analysis.

A series of measurements were performed using the Perkin-Elmer TGS-2 thermogravimetric system in an attempt to determine a good drying temperature. Results are shown in Figures 11-15. Figures 11-13 show the weight loss versus temperature curves for the Kevlar/934 composite, the 934 resin and Kevlar 49 fibers. All these materials were run in air at a flow rate of 50 ml/min, and the temperature was scanned at 10°C/min.

Figure 11 shows the percentage weight loss versus temperature for the wet and dry Kevlar/934 composite. The difference in conditioning is apparent from the weight loss of the two materials, but the difficulty of determining a good drying temperature is also clearly indicated. There is no discernable plateau in the weight loss curves below the onset of resin degradation at 250°C. The only plateau in composite weight occurs between 425 and 525°C, and reflects
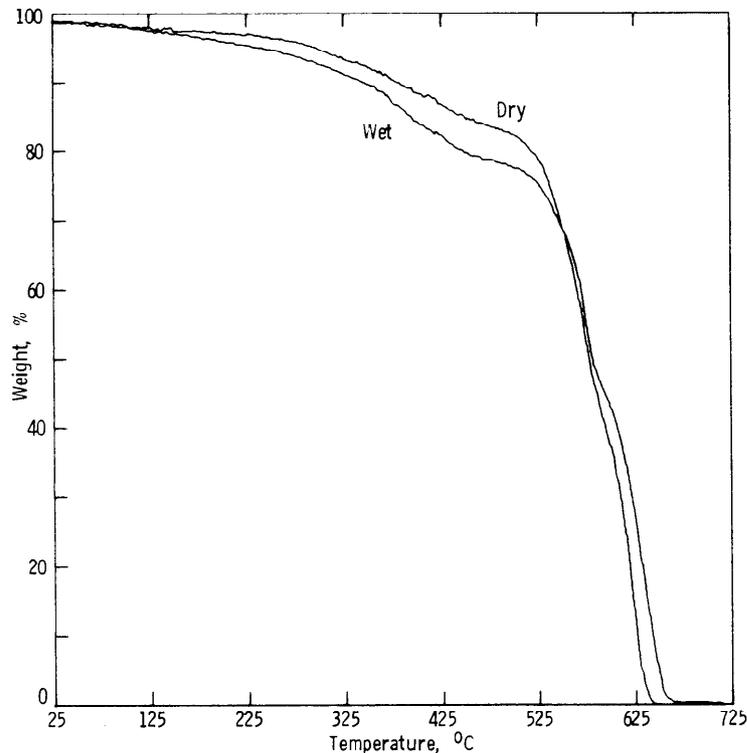
Figure 11 - Thermogravimetric analysis (TGA) of

wet and dry Kevlar/934 composite.

stabilization of the resin char at a weight loss of 10-20%.

Up to 250°C the dry composite loses very little weight and

the wet composite loses perhaps 5%, with the rate of weight

loss accelerating above the wet glass transition of 150°C.

The dry glass transition temperature is approximately 205°C.

The difference between the weight loss of the wet and dry

composite persists and even increases up to 550°C.

The weight loss curves for the resin and the fiber alone

are shown in Figures 12 and 13. The resin curves in Figure
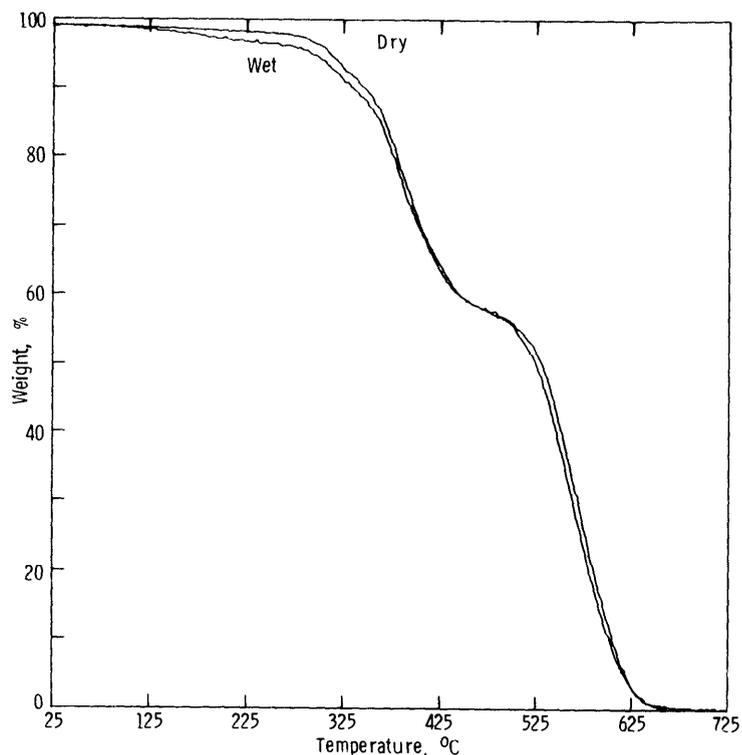
Figure 12 - TGA of wet and dry neat resin.

12 were not obtained on equilibrated specimens (equilibrium
of the 0.10" thick resin plaques takes much longer than for
the laminates), but the differences due to moisture content
are still apparent. Again, no plateau region is discernable
below 250°C, where the pyrolytic process which forms the
resin char begins. The thermooxidative degradation of this
char occurs between 500 and 600°C. The weight loss for the
Kevlar 49 fibers in Figure 13 is much better behaved. The
weight loss for this unconditioned fiber bundle drops above
100°C and levels off at 4-5% above 200°C. Since this mate-
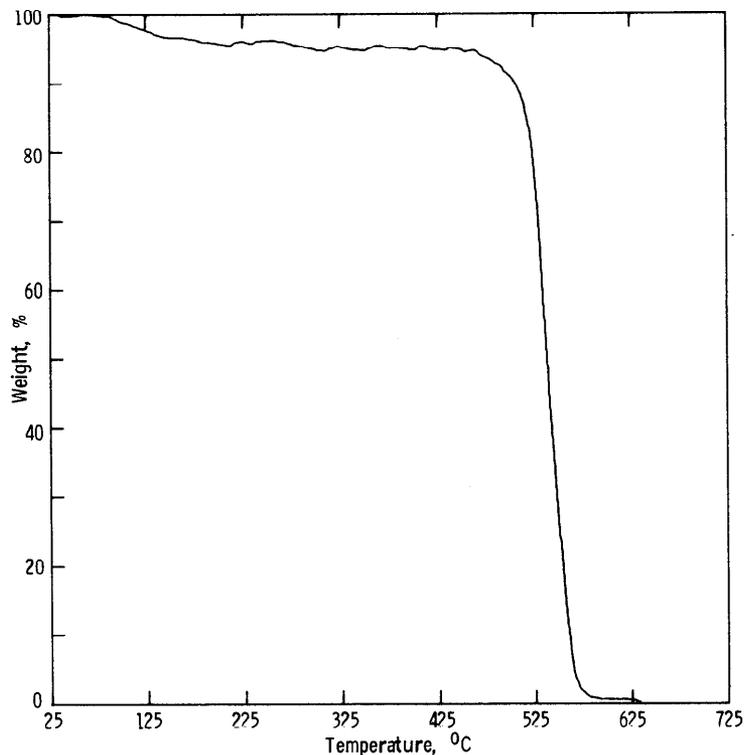
Figure 13 - TGA of Kevlar fibers.

rial is very stable at elevated temperature, no char forma-
tion occurs until the final thermooxidative degradation
between 500 and 600°C.

Both heating rate and atmosphere were varied in an
attempt to improve the situation, and the results are shown
in Figures 14 and 15. Figure 14 shows the weight loss for
the wet composite at 2.5 and 10°C, and Figure 15 shows the
same material run in air and in nitrogen (still 50 ml/min
flow rate) in an attempt to suppress oxidative degradation.
There is no discernable weight plateau in either case.
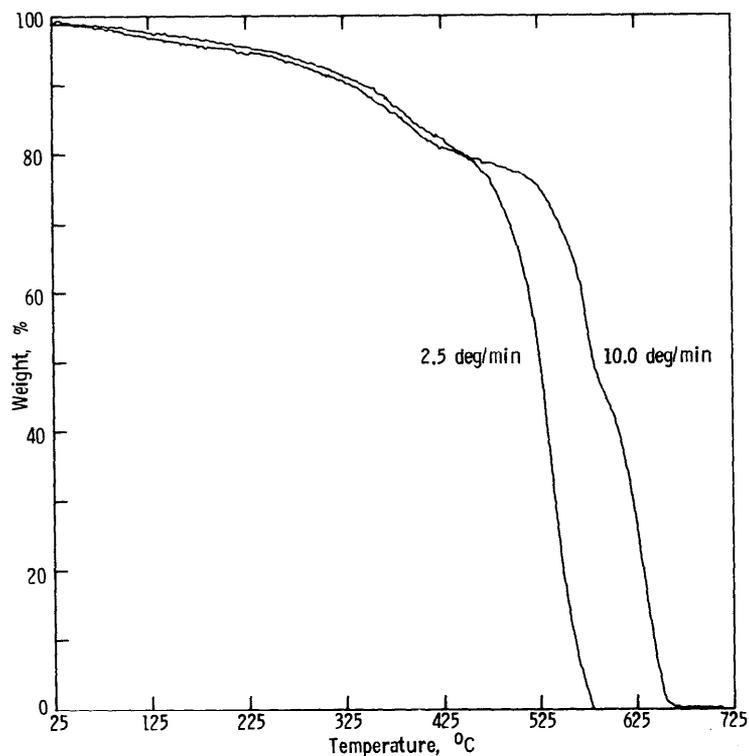
Figure 14 - Effect of scanning rate on TGA
of wet Kevlar/934 composite.

What is required to measure moisture content is some technique which specifically measures moisture driven off the specimen at some temperature under 250°C as a function of hold time. The DuPont 902 Moisture Evolution Analyzer is designed to detect moisture driven off a heated specimen, and considerable effort was made to measure moisture content in the wet and dry composite using it. In this apparatus the specimen is heated in a small furnace in a flowing dry nitrogen carrier gas (100 cc/min). The carrier gas trans-
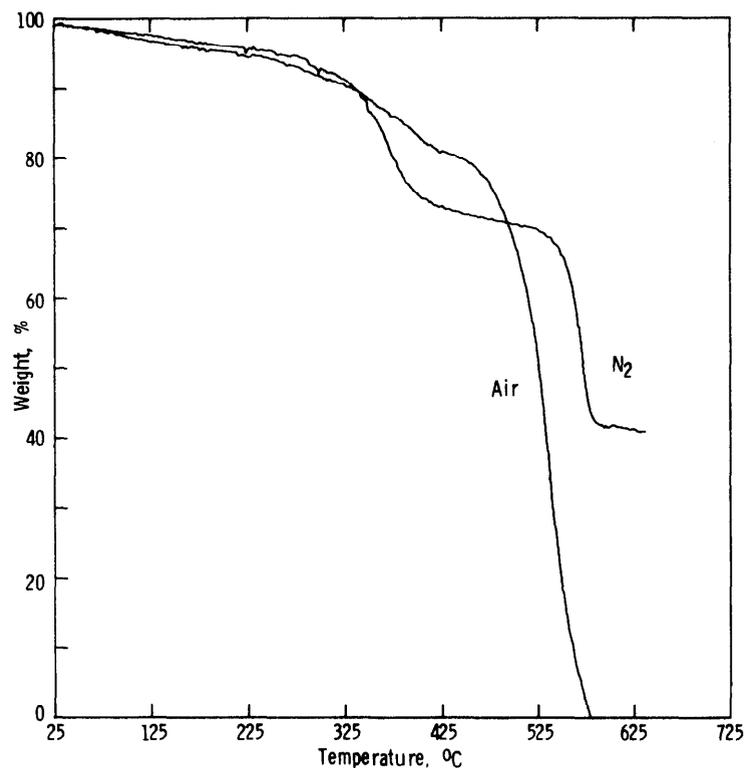
Figure 15 - Effect of atmosphere on TGA of
wet Kevlar/934 composite.

ports the moisture driven off the specimen to an electro-
lytic cell where a thin film of phosphorus pentoxide depos-
ited on the surface of a glass tube absorbs the water. The
absorbed water is then electrolyzed by current flowing
between two helically wound electrodes. The current
required (0.132 microamps per molecule of water) to com-
pletely regenerate the phosphorus pentoxide is integrated
and displayed by the instrument as total moisture content in
micrograms.

All readings which were obtained with the MEA on dry composite indicated moisture contents less than 0.1%. Certain problems associated with the MEA, however, make these measurements less then certainly correct. The instrument is very sensitive to contamination by any volatiles other than water which might be present. After only two or three runs on this material, the instrument would begin to indicate less than the calibration amount of moisture used. All recommended procedures for cleaning and prevention of contamination (e.g. the use of shredded Teflon to filter the carrier gas) were used, but this loss of sensitivity could not be prevented. This instrument had in the past been used with uncured and B-staged resins, and residual volatiles may be difficult to remove.

Also, we were running the MEA measurements at 150 C, which the slowest TGA run (see Figure 14) indicated to be the most promising temperature. Even though there is no assurance that all moisture is removed at this temperature, it is still high enough to drive off low molecular weight components of the original epoxy which might be present in the cured laminate.

All immersion specimens were weighed and dimensionally measured, but this method of studying moisture uptake has a number of limitations. For example, the adhesive tabs must be applied before immersion, and the tabbing material absorbs significant amounts of water. This renders specimen weight a poor indicator of composite moisture uptake.

Weight measurements on small tracer specimens indicate that the moisture content begins to level off at approximately five percent by weight. This occurs in the range of two to three weeks depending on thickness.

C. Torsional Pendulum Analysis.

The technique which was found to be most informative concerning interaction of the material with moisture was torsional pendulum analysis (TPA). This is a form of dynamic mechanical measurement similar to TBA which was discussed in section III. In TPA (see Figure 16), the pendulum element is generally a rigid rod or strip of material, and in this study the mechanical test coupons were used in the TPA without further preparation. In analogy to the TBA, the data obtained are logarithmic decrement and period of oscillation, which in this case can be converted into absolute values of shear modulus, since the specimen geometry is simple.

As was mentioned in section II, the 934 epoxy is strongly plasticized by absorbed moisture, and this is shown in the TPA results given in Figures 17 - 19.

Figure 17 shows a TPA run on the Kevlar/934 laminate after drying at 50°C for one week. The glass transition temperature of this material is clearly indicated by the drop in shear modulus, and by the well defined peak in the decrement. The maximum in loss occurs at 205-210°C, and for the purposes of this study this is considered to be the
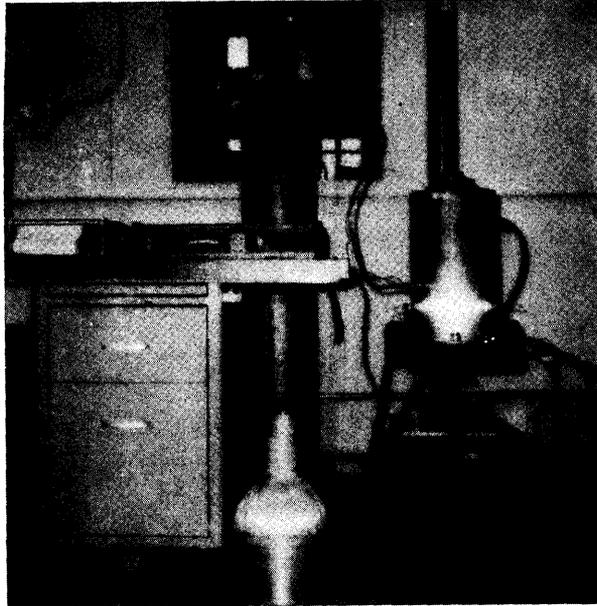
Figure 16 - Torsional pendulum apparatus.

glass transition temperature.   It should   be noted that the

glass transition region begins at approximately $175^{\circ}C$,   very

close to the cure temperature of $177^{\circ}C$.   The TPA curve for

the as-cured   composite is very   similar to the   dried mate-

rial, with a slight shift downward in glass transition temp-

erature.   The   curve for   the material   dried two   weeks is

identical with Figure 17.

This material also exhibits a   well defined low tempera-

ture loss peak at approximately $-50^{\circ}C$.   This peak is noted

by Seferis (27)   in his dynamic mechanical measurements on a
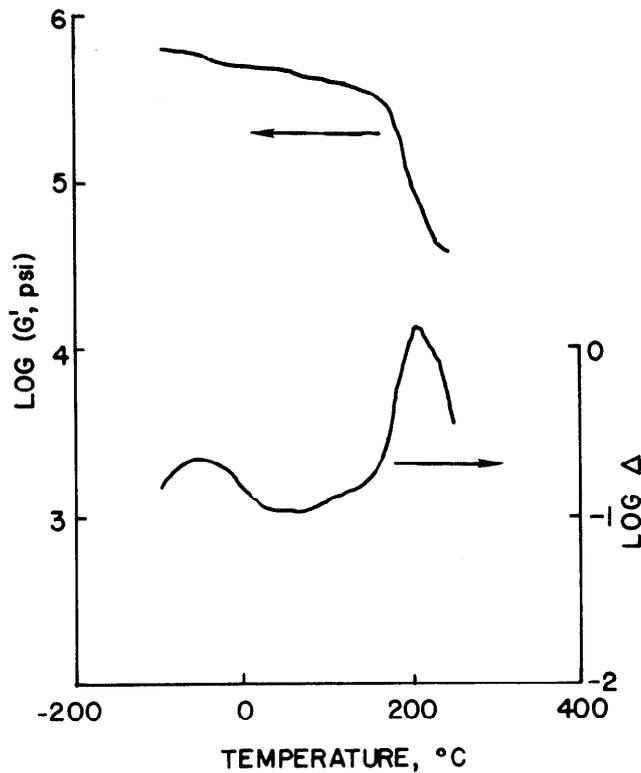
Figure 17 - Torsion pendulum analysis (TPA) of
dry Kevlar/934 laminate specimen.

TGMDA/DDS epoxy. He also observes an intermediate loss
region which shows up in these curves as a weak shoulder on
the glass transition peak.

The effects of moisture absorption are shown in Figures
18-19. After the material has been immersed for one week in
50°C water (Figure 18), the single glass transition peak has
split into two loss maxima, one at 150°C and the other at
200 C. At one week the 200°C maximum is generally higher
than the one at 150°C. The TPA curve after two to three
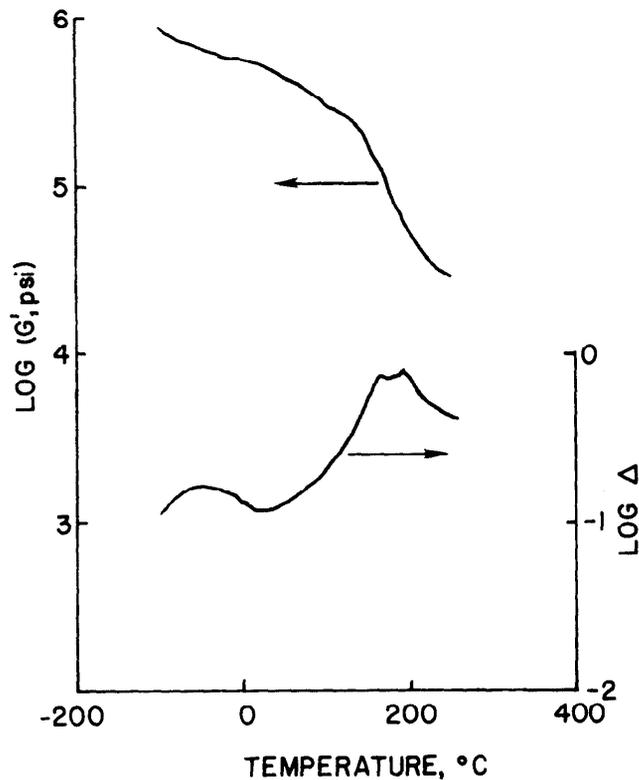
Figure 18 - TPA of Kevlar/934 laminate specimen
after one week immersion.

weeks is shown in Figure 19.   At this point the weight gain

is beginning to level off,   and the loss maximum at 150°C is

clearly predominant, especially in the behavior of the shear

modulus as a function of temperature.   Strength and stiff-

ness measurements as a function of temperature, or TMA meas-

urements would   indicate a glass transition   temperature of

150°C for this material.   Allred (28)   has reported a glass

transition   temperature   of   150°C   for   a   saturated   Kev-

lar/TGMDA-DDS compositee from TMA.   Therefore, the TPA data
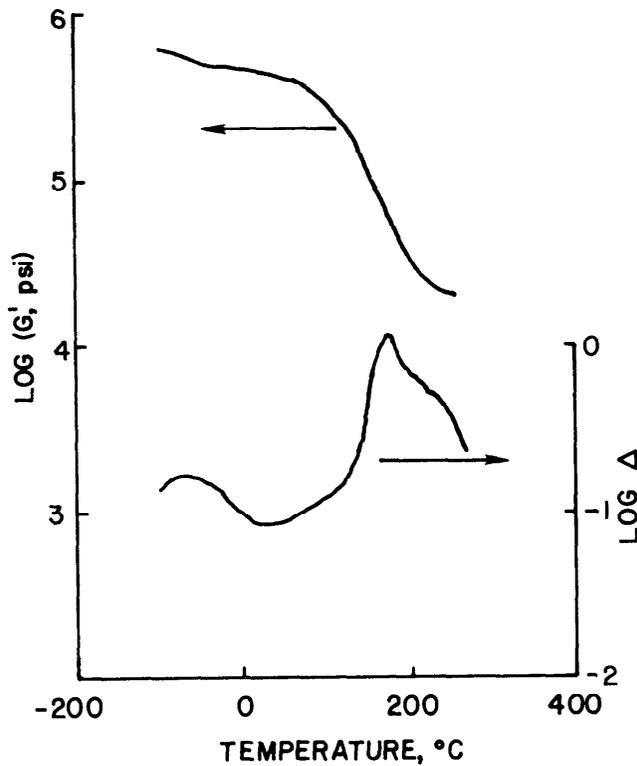
Figure 19 - TPA of Kevlar/934 laminate specimen
after two to three weeks immersion.

indicate that the matrix, at least, is saturated after two
to three weeks immersion. The cooldown curve in both fig-
ures is identical to that of the original dry material in
Figure 17. This indicates that the material is dried but
not seriously degraded by heating to 250°C, although the
surface of the coupon is generally darkened after testing.

The TPA curves for six and eight weeks show no further
changes in dynamic mechanical behavior after three weeks,
although the weight continues to increase very slowly during

this time. Even after three or four months of immersion the TPA curves are unchanged. There is some persistence of the loss maximum of 200°C, and the curve is always broadened toward the high temperature end of the transition region. Some of this broadening, but probably not all, is due to the fact that the specimen is being dried at the surface as it is heated.

These data are quite informative about the nature of the interaction of these laminate specimens with distilled water. The process of diffusion of moisture through the thickness of the material is reflected in the occurence of the bimodal glass transition. This results from saturation of the material at the surface of the specimen and resulting depression of the glass temperature. The material in the interior of the specimen has yet to be reached by moisture and exhibits a glass temperature of 200°C.

The TPA and weight data indicate that these specimens approach equilibrium after three weeks of immersion. There are no literature data on the diffusion rates in this particular composite for comparison, but there are data available on diffusion in TGMDA-DDS epoxies (29). Although there is considerable variability, perhaps due to differences in supplier, Browning (30) has reported data specifically for Fiberite 934 at 50°C. He reports a Fickian diffusion constant of $D = 2.17 \times 10^{-9}$ cm /sec. Assuming Fickian diffusion, the time dependent moisture content of a flat plate immersed in water is of the form:

$$\frac{M_t}{M_\infty} = \frac{4}{L} \sqrt{\frac{Dt}{\pi}}$$

where L is thickness and M is equilibrium moisture content.

The prediction of moisture uptake assuming Fickian diffusion at $D = 2.17 \times 10^{-9}$ for a sheet 0.040" thick with an equilibrium moisture content of 5% is shown in Figure 20. Three weeks is approximately 500 hours, and is marked on the
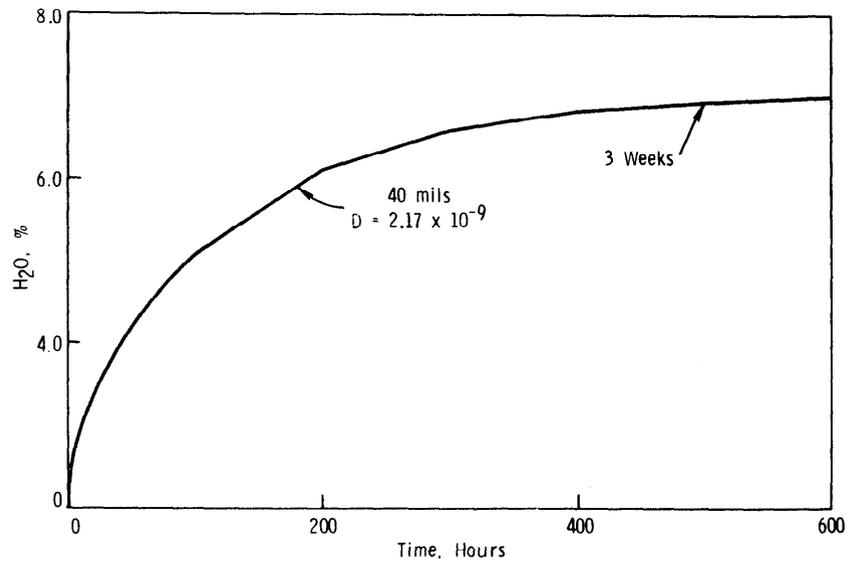
Figure 20 - Weight gain due to Fickian diffusion in a material with $D = 2.17 \times 10^{-9}$, a thickness of 0.040", and an equilibrium moisture content of 5%.

sorption curve.

Although a careful study of the kinetics of moisture uptake in these materials was not within the scope of this thesis, our measurements of uptake on composite tracer specimens indicate that it is nonlinear with respect to root time, even at very short times. Comparison of the uptake data with Fickian analysis could therefore be misleading.

There is also some FTIR evidence that systems with unreacted epoxide may undergo chemical reaction with absorbed water, thereby further complicating the weight gain behavior. This type of reaction might be responsible for the very slow weight gain observed in this and other partially unreacted epoxies at very long times.

The presence of the Kevlar fibers would be expected to slow the diffusion. According to Augl (31), the radial diffusion coefficient for the Kevlar fibers should be perhaps two orders of magnitude less than that of the 934 resin. Augl concludes that the Kevlar fibers would not contribute to moisture transport, but would contribute to moisture content.

The extent to which the Kevlar fibers would slow diffusion through the resin can be investigated analytically using finite element techniques (32). It depends strongly on fiber volume fraction and on local geometrical effects such as fiber-fiber contact.

An upper bound might be estimated using Allred's data (33) on diffusion in quasi-isotropic laminates of 181-weave

Kevlar cloth in a TGMDA-DDS epoxy. He finds the diffusion rate to be approximately one fourth of that of the resin.

A careful experimental study of diffusion kinetics in this system in conjunction with finite element analysis is now underway, and is a very interesting area for future investigation.

The persistence of unchanging high temperature broadening of the glass transition loss peak after up to four months immersion may argue for the presence of an inhomogeneous microstructure in this material. This theory has been advanced by Morgan (29) and others on the basis of scanning electron microscopy of fracture surfaces. They postulate highly crosslinked particles in a less highly crosslinked continuum. These particles would be more resistant to swelling and suppression of the glass transition than the surrounding material.

Another possible explanation for high loss levels between 100°C and 200°C in the wet composite is the presence of a "water peak" in the Kevlar fibers in this range, analogous to the beta transition in nylon 6,6 (34). Dry nylon exhibits low loss levels in the temperature range from -100°C to -50°C, but a loss peak is observed in material containing moisture whose magnitude is proportional to the moisture content. One explanation advanced to explain this phenomenon is that water molecules break up hydrogen bonding and associate themselves with carbonyl groups. This polymer-water side group is thought to give rise to the nylon

beta transition.

In nylon, the moisture is thought to be absorbed only in the amorphous portion of the polymer. Kevlar has no amorphous portion per se, but absorbs 5-6% by weight of water, although this amount is reported to depend upon sodium sulfate content, as discussed in section II. It is not likely, in view of these facts that the interaction of Kevlar with moisture would be similar to that of nylon 6,6, but there were no data available in the literature concerning the dynamic mechanical properties of Kevlar. Therefore, a series of dynamic mechanical measurements on wet and dry Kevlar fibers was performed to examine the possibility of a "water peak" between $100^{\circ}C$ and $200^{\circ}C$. A Rheovibron DDV-II was used for these measurements, with a dry nitrogen purge for the dry fiber and a stream of saturated air for the wet fibers. In measurements up to $250^{\circ}C$ the dynamic mechanical behavior of the Kevlar fibers was completely featureless, wet and dry.

These measurements are difficult due to the extremely high modulus and low loss of the fibers, as well as the thermal shrinkage which occurs as the fibers are heated. The results certainly fail to indicate any water peak, however, and any loss maxima in the temperature range from room temperature to $250^{\circ}C$ are most surely due to the 934 resin, and not the Kevlar fiber.

The importance of moisture induced changes in the 934 resin can be seen in the next section on the effects of

differing moisture content on the mechanical properties of the Kevlar/934 composite.

V. MECHANICAL PROPERTIES

A number of different tests were performed to study the effects of moisture on the mechanical properties of the Kevlar/934 laminates. These included quasi-static tensile tests on a variety of specimens, quasi-static flexural tests and tension-tension fatigue. The properties of the Kevlar fibers and unreinforced 934 epoxy resin were also studied as a function of conditioning. In the following section, mean values, number of tests, and coefficients of variation are reported in the data tables. The data from which these statistical summaries were computed are included in the Appendix.

A. Tensile Tests.

1. Tensile Testing of Kevlar/934 Laminates.

The 2'x4' unidirectional laminates, fabricated as described in section III, were first cut into five 2'x8.5" sections labeled A-E, using a circular saw. Each of these sections was then cut into 8.5"x0.5" strips using a water cooled diamond wheel. A number of different specimens were fabricated from these 8.5"x0.5" strips. The first and most simple was a modification of the ASTM D3039 specimen which calls for tabs or doublers to be bonded adhesively to the ends of a straight strip. This type of specimen worked fairly well for simple tensile tests, although axial splitting of these materials at failure almost always runs up

into the grip area.   When the D3039 specimen was used for
tension-tension fatigue tests, however,   serious problems
were encountered.   Under almost all conditions of fatigue
loading, the adhesive bond between the composite and the
doubler failed before the material failed.   This problem is
made more severe by the environmental conditioning.   The
test method which was developed as an alternative was simply
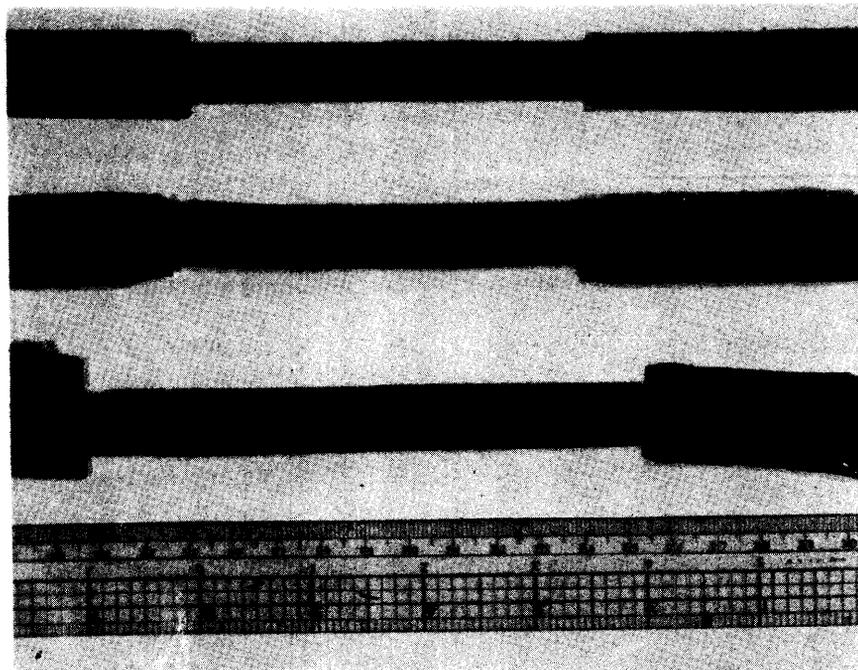
Figure 21 - Straight-strip tensile specimens.

Top - an untested specimen.

Middle and bottom - typical failures

of dry and wet specimens respectively.

to leave out the doubler (see Figure 21).

The ends of the strips are lightly sanded and cleaned

with acetone.   Two layers of the   film adhesive   (in this
case, American Cyanamid FM123)   are then applied to the ends
of the strips in 2.5" wide pieces,   extending approximately
0.5" beyond the sanded area.   These "adhesive tabs" are then
cured for one hour at 100°C and 100 psi.   Under these condi-
tions the adhesive is somewhat undercured, but these tabs
appear to minimize slippage in the grips.   If these adhesive
tabs are applied before drying as described in section IV,
they are embrittled during drying and tend to delaminate
from the surface of the strip during testing.   No similar
problems occur with tabbed immersion specimens until approx-
imately two months at 50°C, which is beyond the time of con-
ditioning for these tests.

A large number of these quasi-static specimens have been
tested in tension, dry and wet.   Most tests were performed
at 0.02"/min deformation rate, although twelve dry specimens
were used to study the effect of deformation rate on the
measured strength.   This is necessary in order to compare
the results of the quasi-static tests with those of the
cyclic tests which were performed at 10 Hz.

Tests were performed on the dry specimens at 0.005,
0.05, 0.5 and 5.0"/min deformation rate.   No consistent
effect of rate was observed on the strength in this range.
The results of the quasi-static tensile tests on the Kev-
lar/934 0.5" straight strips are shown in Table II.   Ulti-
mate tensile strength is denoted "UTS" and Ei and Ef are
initial and final tangent modulus, respectively.

TABLE II

TENSILE TESTS ON KEVLAR/934 LAMINATES

	Dry	Wet
UTS, kpsi	180.0 (15,6.3%)*	207.2 (14,11.3%)
Ei, Mpsi	11.12 (6,6.8%)	10.8 (5,2.5%)
Ef, Mpsi	13.0 (6,7.4%)	13.0 (5,4.4%)
ϵf,%	1.6 (6,0.5%)	1.8 (5,4.5%)

The wet specimens tended to undergo more extensive axial
cracking during tensile loading than did the dry specimens
(see Figure 21). Typical stress-strain curves for the wet
and dry strip specimens are shown in Figure 22.

Since considerable variability is observed in the
strengths determined by this method, and since the increase
in the strength was not expected, similar tests were run on
a newly developed test specimen called a "streamline" speci-
men. This specimen was developed by D. Oplinger at the Army
Materials and Mechanics Research Center. The design mini-
mizes the ratio of shear stress to tensile stress, and
avoids maxima in tensile stress in the region of expanding
cross section. High values of the ratio of shear to tensile
stress causes localized shear failures at the neck region of
the standard D638 dogbone specimen. The streamline design
(35) is based on an analogy between hydraulic flow and elas-
tic stress fields in bodies of comparable shape. In this

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* Values in parentheses indicate number of tests and per-
  centage coefficient of variation.
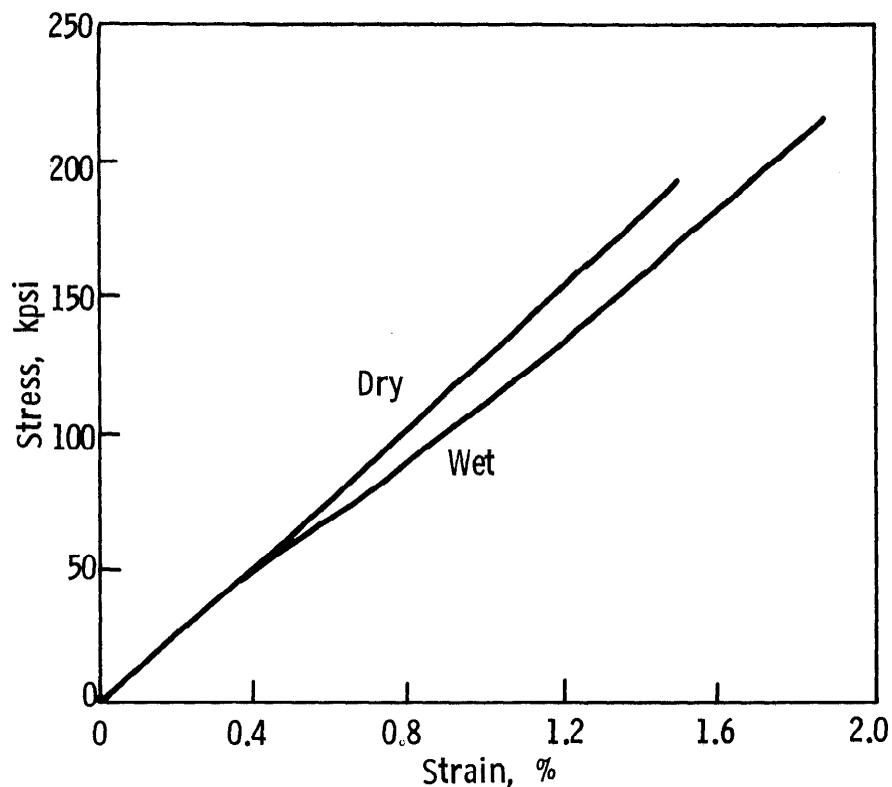
Figure 22 - Typical stress-strain curves for wet and dry
strip specimens.

case the analogy is drawn with two-dimensional flow in a channel with an abrupt right-angles expansion. The shape of the flow lines in this case have been calculated in closed form and are shown in Figure 23. The parameter ρ refers to the final position of the flow line between the upper and lower boundaries of the expanded section. It can be shown that shapes corresponding to ρ less than or equal to 0.5 eliminate intermediate maxima in tensile stress in the region of expanding cross section. For ρ less than 0.4 the
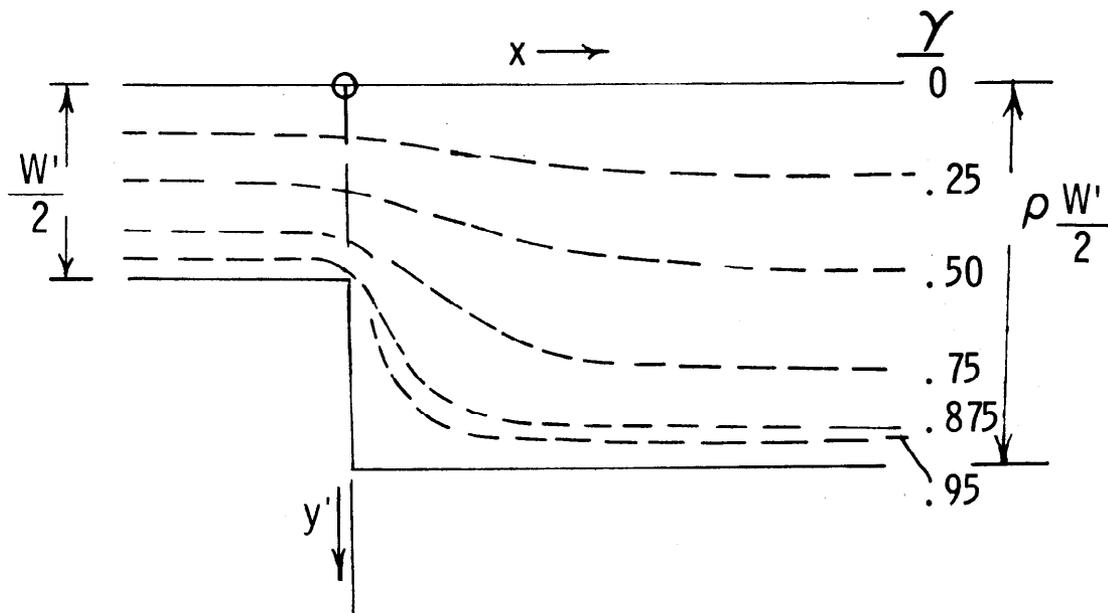
Figure 23 - Design of streamline tensile specimens (35).

shear stress is less than approximately 6% of the nominal tensile stress in the gage section. The streamline specimens used in this study used $\rho=0.4$. In the absence of laser or water jet machining equipment, these specimens were prepared using a modification of a Pentograph machine. The technique involves clamping one of the 0.5" straight strips in the machine and cutting the strip down to the streamline configuration of a selected template. A router head is used, operated by a stylus which is moved around the outside of the template.

We have found that the Kevlar/934 streamline specimens require the FM123 adhesive tabs to prevent slipping in the grips. The tabs are not necessary on similar specimens of

glass/epoxy or graphite/epoxy, however. The tabs were applied to the streamline specimens in the same way as to the straight strip specimens.

In general, failures in these streamline specimens initiate well away from the grips (see Figure 24), and this eliminates failure due to stress concentrations at the grips. Such failures might be differently affected by
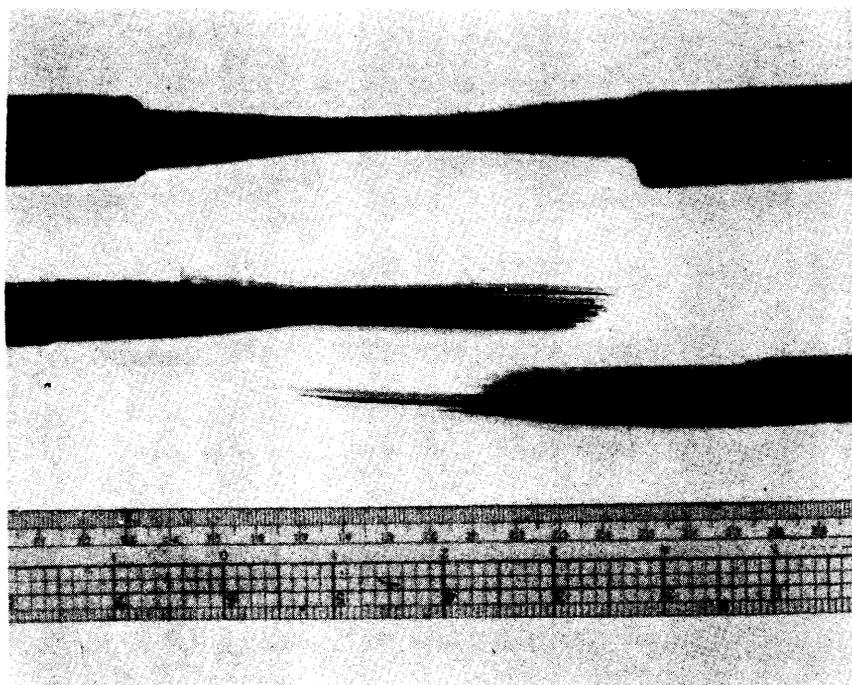
Figure 24 - Streamline tensile specimen and
typical failure of a wet streamline specimen.

absorbed moisture than failure in the bulk of the material. The results of the tests of these streamline specimens are shown in Table III. These data were obtained at 0.02"/min

deformation rate.

TABLE III

TENSILE TESTS ON KEVLAR/934 STREAMLINE SPECIMENS

Conditioning	UTS, kpsi
Wet	230 (6,4.6%)
Dry	210 (6,1.6%)

To study the effect of absorbed moisture on the Kevlar fiber and the unreinforced 934 resin, tensile tests were also performed on these materials as a function of conditioning.

2. Tensile Tests on Kevlar Fibers.

A series of measurements on various fiber specimens were performed using the Instron pneumatically operated tire cord grips. The specimens were gripped in capstan grips triggered when the specimen reaches a preset level of tension. Tests were also performed using a tabbed specimen configuration. Here the ends of the yarn are glued between two heavy cardboard tabs as shown in Figure 25. The yarns were glued into the tabs using "Epoxi-patch" epoxy, cured for twenty four hours at 50°C.

For some of the measurements, attempts were made to extract Kevlar fibers from the prepreg for testing. A strip of prepreg was removed and soaked in acetone until the fibers appeared clean. The fibers were then removed, dried, and weighed to determine denier and tested. As noted in the
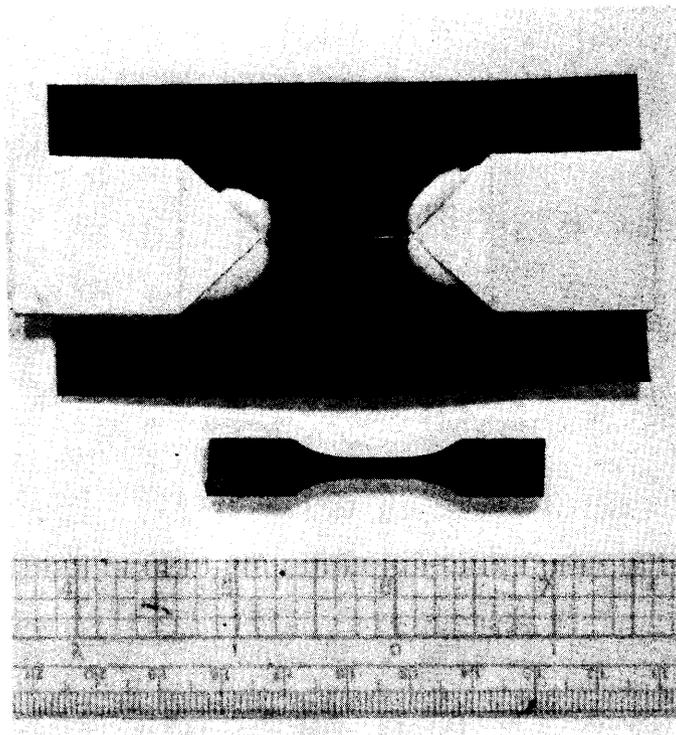
Figure 25 - Fiber and epoxy tensile specimens.

section on liquid chromatography, it is difficult to remove all of the resin from the prepreg fibers, and despite lengthy soaking in acetone the fibers were always somewhat stiff when dried.

Mean strengths of unconditioned fibers obtained from the Kevlar/934 prepreg in this way were fairly low (approximately 11.09 gm/den, or 204.1 kpsi). It is possible that the fibers are damaged by removal from the prepreg. Tests as a function of moisture content were therefore performed on separate 195 denier yarns, obtained directly from DuPont.

The wet yarns were immersed in 50°C distilled water for one week, and the dried yarns were held for one week in a vacuum oven at 50°C. Given the diameter (approximately

0.005") of the fibers and the reported diffusion constant of approximately 2×10^{-9} (cm/s), the fibers should be equilibriated under these conditions.

A gage length of 7" and a deformation rate of 5"/min. were employed with the specimens tested with the capstan grips. The tabbed specimens had a gage length of 1", and were tested using a servohydraulic Instron Model 1331, at a ramp rate of 20 Hz, corresponding to a cyclic frequency of 10 Hz, which was used for the fatigue tests, and also at a deformation rate of 0.005"/min, corresponding to the strain rate used in laminate testing. The measured strengths were not sensitive to rate of loading. Results of the fiber tests are shown in Table IV. Tabbed specimen data shown here are for 0.005"/min.

TABLE IV.

TENSILE PROPERTIES OF KEVLAR FIBERS

Fiber	Specimen	Cond	Tenacity, kpsi
Prepreg	Capstan	unc	204.1 (8,14.9%)
195d yarn	"	unc	307.7 (20, 14.0%)
"	"	wet	334.6 (20,13.0%)
"	"	dry	279.5 (20,14.0%)
"	Tabbed	dry	368.8 (8,9.3%)
"	"	wet	370.1 (8,5.8%)

It should be noted that the wet untabbed yarn specimens were not dried before testing. The water lubricated the yarns, making them easier to handle than the dried fiber

specimens.   This probably accounts for the apparent higher

strength of the wet yarns,   since such an effect is not in

agreement with data reported elsewhere (23).   This is made

more likely in view of the fact that much higher strengths

are obtained with the tabbed specimens, casting doubt on the

validity of the strengths obtained using capstan grips. The

modulus of the yarns as measured with the tabbed specimens

was 15-16 Mpsi in both wet and dry material, and was appar-

ently linear up to the failure stress.   The strengths

obtained with the tabbed fiber specimen were higher than

those obtained with the capstan grips, although the distrib-

ution of strengths is skewed to the high strength end. When

additional care was taken with specimen preparation, some of

the lower stress failures were eliminated, but the distrib-

ution of strengths is still fairly broad.

One variable in the tabbed specimen which had to be

carefully controlled was the extent of wicking of the epoxy

resin into the yarn.   This wicking resulted from curing of

the epoxy at elevated temperature before sufficient time

(3-4 hours) was allowed for room temperature cure.   If such

wicking was visually apparent, the tensile strength

increased, but the fatigue resistance was degraded.

3. Tensile Tests on 934 Epoxy.

Tests were performed as a function of conditioning on

ASTM D1822 tensile specimens machined from plaques cast from

the 934 epoxy (see Figure 25).   The epoxy plaques were

prepared using a technique based upon recommendations from Fiberite: 1) Treat mold with release agent and preheat mold and 100% resin solids to 65°C (150°F). 2) Pour resin into mold in vacuum oven at 60 °C. 3) Cycle the vacuum until foaming subsides and then hold at full vacuum. 4) Heat oven to 100 C (212 F) and hold ten hours (overnight). 5) Heat oven to 162 C (325 F) and hold two hours. 6) Cool slowly.

The degree of cure of these plaques was characterized by FTIR as discussed in section III. It was found to be the same as that of the epoxy in the Kevlar/934 laminates.

These plaques were approximately 0.1" thick. The small tensile specimens which were machined from them were conditioned in the same manner as the laminate specimens, and for the same length of time. As a result of the greater thickness, these specimens were not at equilibrium when tested after two to three weeks. The difference in moisture content between the wet and dry specimens was approximately 3%.

In an attempt to measure the properties of the saturated resin, a set of specimens from another plate was conditioned in 80°C distilled water. At this temperature, the reported diffusion coefficient is greater than $2x10^{-7}$ cm /s (31), and these resin specimens would reach equilibrium after two weeks of immersion. The moisture uptake at eighteen days was approximately 7%. This is greater than that reported for equilibrium with 100% relative himidity. This suggests that the matrix is saturated and liquid water is present in the voids. These specimens were removed from the water and

tested after eighteen days.

The tensile tests were performed at 0.02"/min deformation rate. The results are shown in Table V.

TABLE V.

TENSILE TESTS ON 934 EPOXY

Cond.	UTS, kpsi	E, kpsi	ϵf, %
dry	10.9 (5,19.4%)	598 (5,2.5%)	2.3 (5,26%)
wet	9.08 (6,8.8%)	510 (6,3.5%)	2.2 (6,9.5%)
80°C	7.15 (7,9.5%)	529 (7,5.3%)	1.5 (7,11%)

The stress-strain behavior of the resin specimens is nonlinear, with the modulus decreasing at higher stress. The nonlinearity becomes apparent at lower stress in the wet material. This is in agreement with Morgan and O'Neal on TGMDA/DDS epoxy (25). They report the stress at the onset of nonlinearity to be 5% lower in the wet material than the dry at room temperature. They assert that this stress is associated with localized flow.

Ductility in the sense of increased macroscopic strain to failure is not enhanced by moisture absorption in these tensile tests. The wet material is clearly softer, however, and under a stress state other than uniaxial tension which suppresses brittle fracture by crack propagation the softer material might be expected to undergo more extensive flow.

Since TPA data indicate that this epoxy is strongly plasticized by absorbed moisture, the differences between the wet and dry epoxy should be greater at elevated

temperatures.   This is indicated by literature data on this material (25).

B. Compression Tests on 934 Epoxy Resin.

Since brittle fracture in tension occurs before yield in both wet and dry resin, compression testing was performed to observe the yield and and flow behavior of the resin as a function of moisture content. The resin was tested dry, and after eighteen days at 80°C in distilled water. The compression specimens were 0.25" high by 0.25" wide and 0.1" thick. They were tested at 0.05"/minute deformation rate. The results are shown in Table VI, and typical compression stress-strain curves are shown in Figure 26.

TABLE VI.

COMPRESSION TESTS ON 934 EPOXY.

	Wet	Dry
E_i, kpsi	362 (6,2.6%)	393 (6,4.1%)
σy, kpsi	17.4 (6,1.1%)	29.4 (6,2.7%)
ϵy, %	9.4 (6,4.6%)	12.3 (6,3.3%)
σf, kpsi	39.1 (6,7.9%)	39.7 (6,14.3%)
ϵf, %	47.0 (6,2.5%)	35.6 (6,25.8%)

Although the initial moduli of the wet and dry resin are similar, the onset of nonlinearity occurs at a much lower stress in the wet resin, and the yield stress of the wet resin is approximately 50% that of the dry resin.

Clearly, moisture absorption not only depresses the
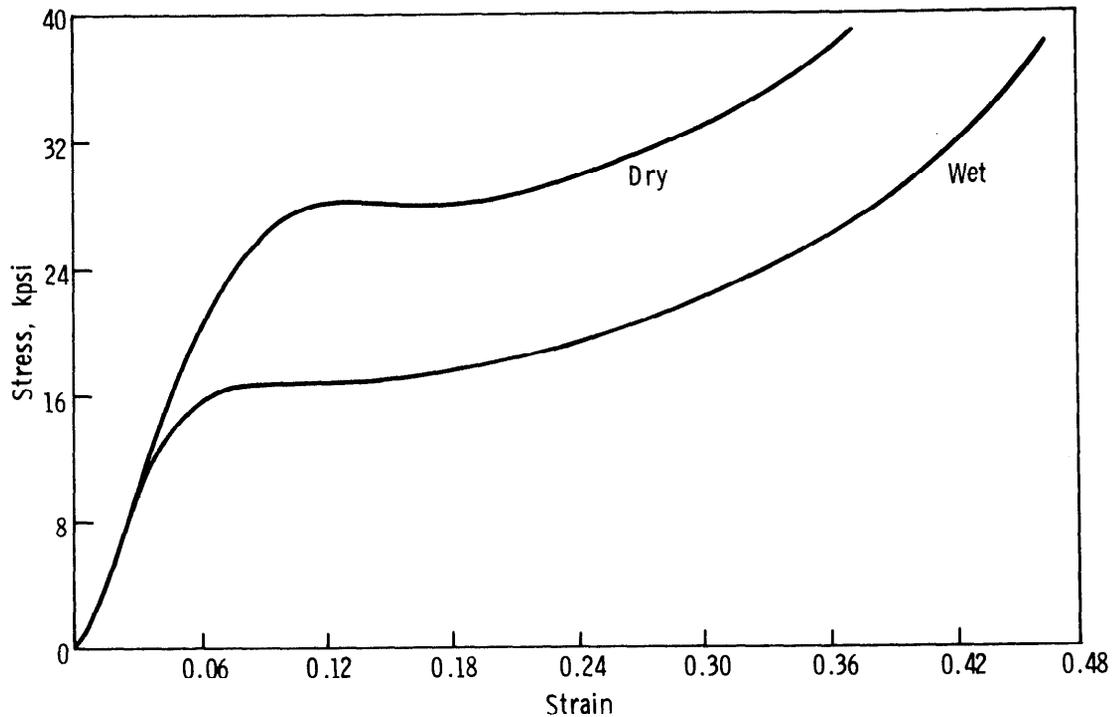
Figure 26 - Typical compression stress-strain curves for wet and dry resin.

glass transition temperature of this epoxy, but has a significant effect on its yield and flow behavior as well.

C. Flexure Testing of Kevlar/934 Laminates.

The flexural strength and stiffness of the Kevlar/934 laminates were also measured as a function of moisture content. The method employed was ASTM D790, which prescribes procedures for three-point bending tests. The 0.5" strips were used, with a span of 2" and a deformation rate of

0.2"/min.   The results of these tests are shown in Table
VII.

TABLE VII.

FLEXURE TESTS ON KEVLAR/934 LAMINATES.

Cond	Flex. Strength, kpsi	Flex. Stiffness, Mpsi
unc.	82.4 (46,2.9%)	8.93 (46,4.2%)
wet	75.0 (18,7.4%)	8.34 (16,8.3%)
dry	85.6 (17,3.9%)	8.75 (17,5.4%)

These specimens failed in compression at the upper surface
in all cases.   A series of bands on the top surfaces of the
specimen reflected fiber buckling with a period of approxi-
mately 0.01".

D. Testing of Notched Specimens of Kevlar/934

The resistance of the wet and dry composite to delamina-
tion was investigated by means of tensile testing of notched
0.5" strips.   A micrometer stage was used to control the
depth of the notches.   These must be machined to very close
tolerances, since the failure loads are quite sensitive to
notch depth.   For these tests, the notch depths were one-
half the total laminate thickness.   Water cooling was found
to be necessary to prevent thermal degradation during notch-
ing, so the notched specimens were reconditioned at 80 C for
one week.

The specimen geometry and typical load-deflection curves

are shown in Figure 27.   These specimens were tested in the
Instron TTC tester at 0.02"/min crosshead rate, and deforma-
tion was monitored by a 1" gage length extensometer mounted
on the unnotched side of the specimen, spanning the notch.
Adhesive tabs were found to be necessary to prevent slippage
in the grips.

The load at which delamination initiates is denoted by
Li.   This delamination propagates in both directions at
gradually increasing load until it stabilizes at 2-4% strain
and the load-deformation curve increases markedly in slope.
The specimen fails by tensile failure of the unnotched por-
tion.   Stresses have not been calculated since stresses at
the notch tip are difficult to determine due to high local
stress concentration.   The results of these tests are shown
in Table VIII.

TABLE VIII.

FAILURE LOADS OF NOTCHED KEVLAR/934 LAMINATES.

Condition	L_i, lbs.	L_f, lbs.
Wet	733 (5,2.6%)	1507 (5,4.0%)
Dry	770 (5,2.3%)	1443 (5,6.3%)
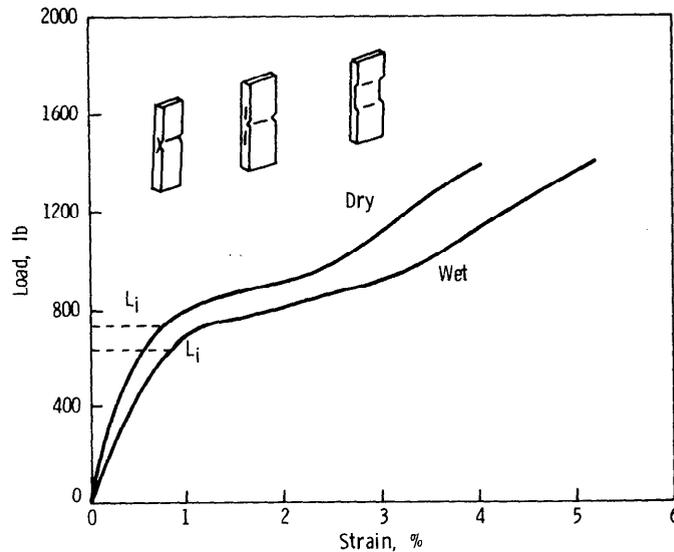
Figure 27 - Geometry and load-deformation behavior of
notched specimens.

E. Fatigue Testing.

1. Fatigue testing of Kevlar/934 Laminates.

The tension-tension fatigue resistance of the Kevlar/934
composite material was studied as a function of moisture
content. The fatigue tests were performed on the adhesive
tab straight strip specimens described in section V.A.1, at
a frequency of 10 Hz and a stress ratio of R=0.1 (this is
the ratio of the minimum to the maximum stress during the
sinusoidal loading cycle). These conditions were chosen to
correspond to the types of fatigue loads commonly encoun-
tered in the blades of rotary wing aircraft (36). This is

an important potential application for Kevlar. The measure-
ments were made on an Instron 1211 cycler shown in Figure
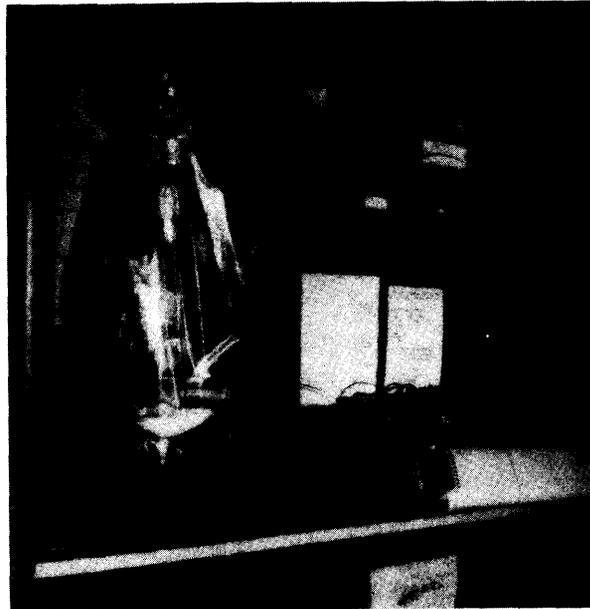
Figure 28 - Instron 1211 fatigue testing machine.

28.

Since many of the fatigue tests lasted up to a week, the
environment of the specimen was controlled during testing.
The dried specimens were enclosed in a sealed polyethylene
bag over anhydrous calcium sulfate desiccant. The wet spec-
imens were enclosed in a sealed polyethylene bag over dis-
tilled water. The temperature of the environment was not
controlled (ambient temperature was 23°C), but considerable

internal heating of the specimens occurred during fatigue

loading.   The specimen temperature was monitored by various

means, including an iron-constantan thermocouple attached to
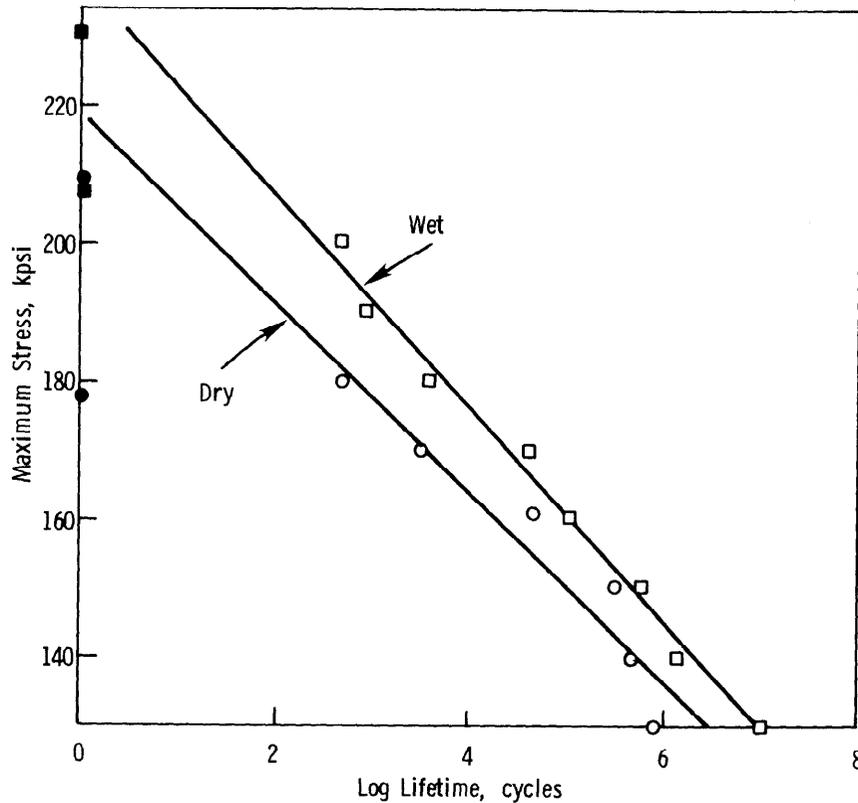
Figure 29 - Tensile S-N curves for wet and dry Kevlar/934.
Closed symbols indicate single cycle strengths.
The higher values of wet (square) and dry (circle) strengths
are for streamline specimens.

the specimen surface and a scanning infrared camera.

The mean log lifetimes as a function of maximum stress

are shown in Figure 29.   Stress (S) is plotted versus the

logarithm of lifetime in cycles (N).   The data presented in

Figure 29 are shown in Table IX.

Least-squares linear regression were performed on each
of these sets of data, and the lines plotted in Figure 29
are the best fit to the data obtained in this way.   Coeffi-
cients are shown in Table X.   The "correlation coefficient"
R is a measure of goodness of fit.

TABLE IX.

MEAN FATIGUE LIFETIMES OF KEVLAR/934 LAMINATES

Maximum tensile stress, kpsi	Mean log lifetime, wet	Mean log lifetime, dry
200	2.690 (3,0.6%)	---
190	2.936 (3,7.7%)	---
180	3.601 (4,14.7%)	2.720 (4,1.2%)
170	4.627 (5,14.0%)	3.533 (5,41.0%)
160	5.060 (4,5.8%)	4.685 (7,19.0%)
150	5.776 (3,1.9%)	5.531 (8,7.3%)
140	6.149 (3,1.9%)	5.690 (5,4.5%)
130	7.020 (3,1.0%)	5.930 (5,6.4%)

TABLE X.

$$S = B(1)*LOG\ N + B(0)$$

Cond	B(0)	B(1)	R
Wet	238.6	-15.56	0.988
Dry	219.6	-13.80	0.922

Single cycle strengths for the standard adhesive-tabbed
specimens used for fatigue testing are shown in Figure 29.

Also indicated are the single-cycle strengths obtained with the streamline specimen.

Macroscopic failure modes observed in the tension-tension fatigue tests were similar to those which occurred in quasi-static tensile tests. Axial splitting occured in both wet and dry specimens, but the splitting was much more extensive and evenly distributed in the wet specimens than in the dry (see Figure 21 for quasistatic failure modes).

Specimen temperature during each fatigue test was recorded using either a strip chart for thermocouple measurements or a videotape system with the scanning infrared camera. Maximum surface temperatures above $100^{\circ}C$ were recorded for tests at the higher stress levels. The shape of the temperature versus time curve was quite reproducible, and an example is shown in Figure 30. These data were obtained on a wet specimen at a maximum stress of 160 kpsi, with an iron-constantan thermocouple securely taped to the middle of the specimen.

The temperature increases quite rapidly after a few seconds, the length of time required for the Instron 1211 cycler to reach maximum load. There is an initially linear increase in temperature, which then levels off and decreases to a stable temperature which is maintained throughout the test. A few hundred cycles before the specimen fails, there is considerable local heating around the point at which the failure initiates. This heating is clearly visible in thermograms, and is of the order shown in Figure 30. An example
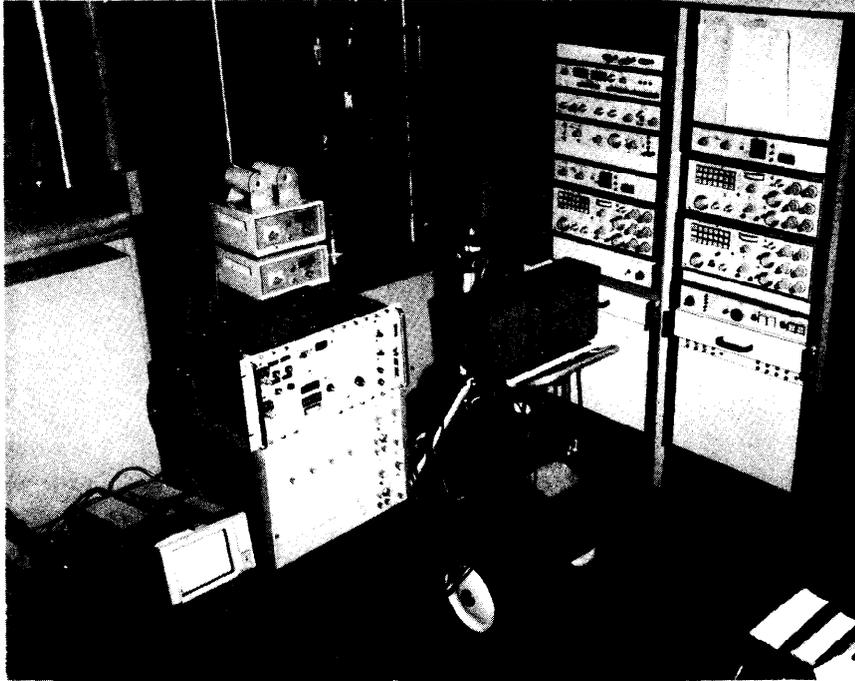
Figure 32 - Inframetrics scanning infrared camera.

thermocouple, which does not give a clear picture of the entire specimen. This variability renders least-squares linear regression a questionable technique for analysis of these data. There is, however, an apparent relationship between initial rate of heat buildup during fatigue loading and the ultimate lifetime of these specimens. If this measurement could be refined with the use of thermographic equipment, heat buildup in composite specimens or components at low cyclic stresses might be used as a nondestructive indication of potential lifetime at higher stress levels.
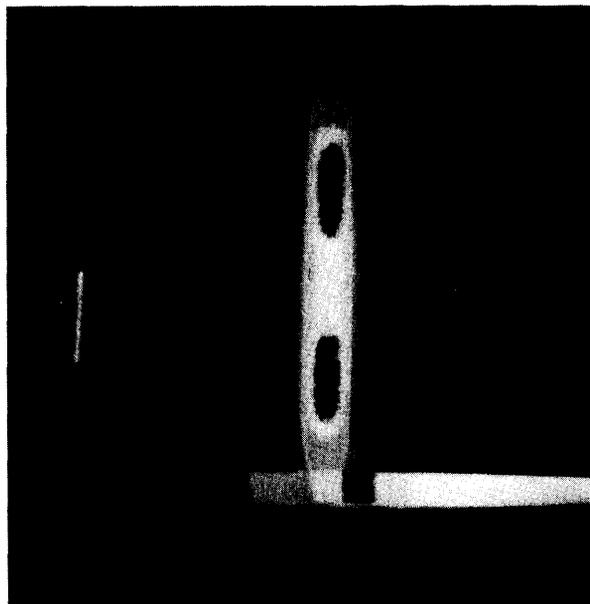
Figure 31 - Thermogram of specimen during fatigue.

with the Instron 1211 cycler.

Figure 33 is a plot of log lifetime versus initial heat-
ing rate (indicated in Figure 30) for wet Kevlar/934 speci-
mens.   All these data were obtained using a thermocouple.
At the highest maximum stress level used, 200 kpsi, the
specimens generally failed before any noticeable temperature
increase.   There is considerable scatter in these data, per-
haps due to inadequacies inherent in the use of the

----

* Inframetrics,   Inc.,   25 Wiggins Avenue,   Bedford,   Mass.
  01730
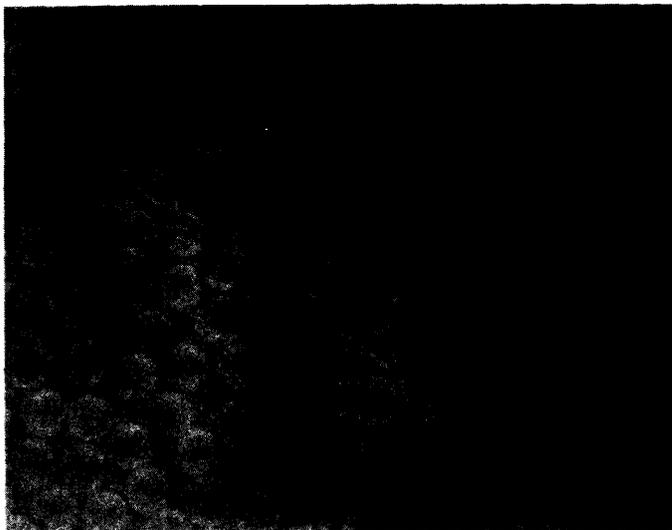
Figure 34a - Fatigue crack in Kevlar/934 laminate.
Crack runs predominantly through Kevlar fibers.

stable manner throughout much of the time under fatigue load. Figures 34b&c show scanning electron micrographs of a specimen which failed in fatigue. Figure 34b shows a fracture surface apparently damaged by cyclic loading. Figure 34c shows a broken fiber with axial splitting.
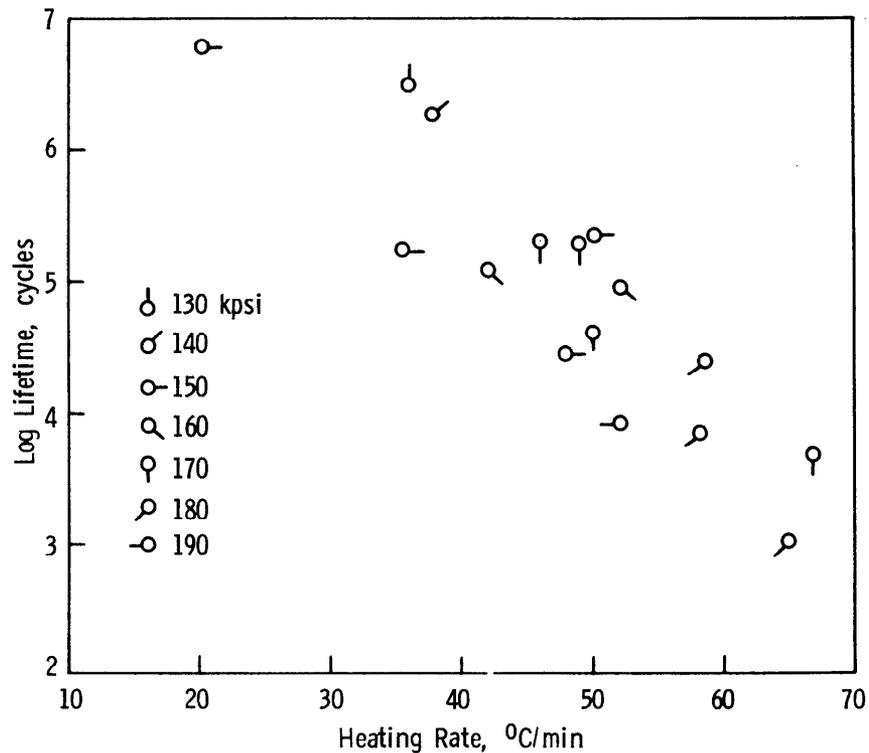
Figure 33 - Log lifetime of wet Kevlar/934 laminates as a function of initial heating rate during fatigue loading.

Various types of failure which occur during fatigue loading of the Kevlar/934 are shown in Figure 34. Figure 34A is an optical micrograph of a polished section of an unconditioned specimen which was loaded 100,000 cycles at 130 kpsi. It shows a fatigue crack propagating preferentially through the fibers. The considerable length which these cracks attain in the sectioned surface of these fatigue specimens suggests that the cracks propagate in a
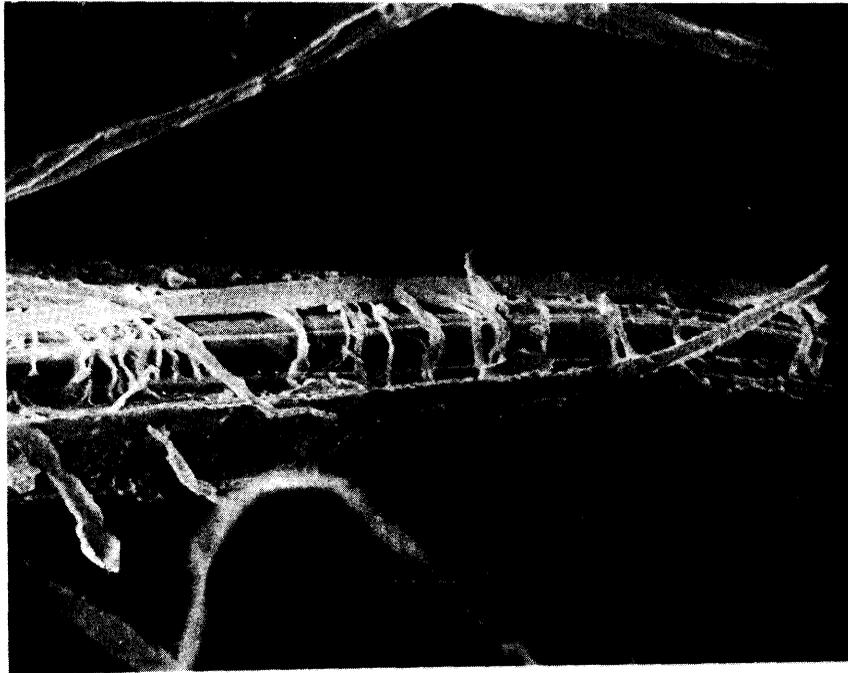
Figure 34c - Fiber damaged during fatigue fracture in Kev-
lar/934.

2. Fatigue Testing of Kevlar Fibers.

To investigate the mechanism of fatigue failure in these
composite specimens, the fatigue resistance of the Kevlar
fibers was also studied. If the rate of loss of strength
during fatigue loading were the same for the fibers alone as
for the composite, then the fatigue behavior of the laminate
could be explained only in terms of the fiber properties.
Clearly this is not the case, as is shown in Figure 35, the
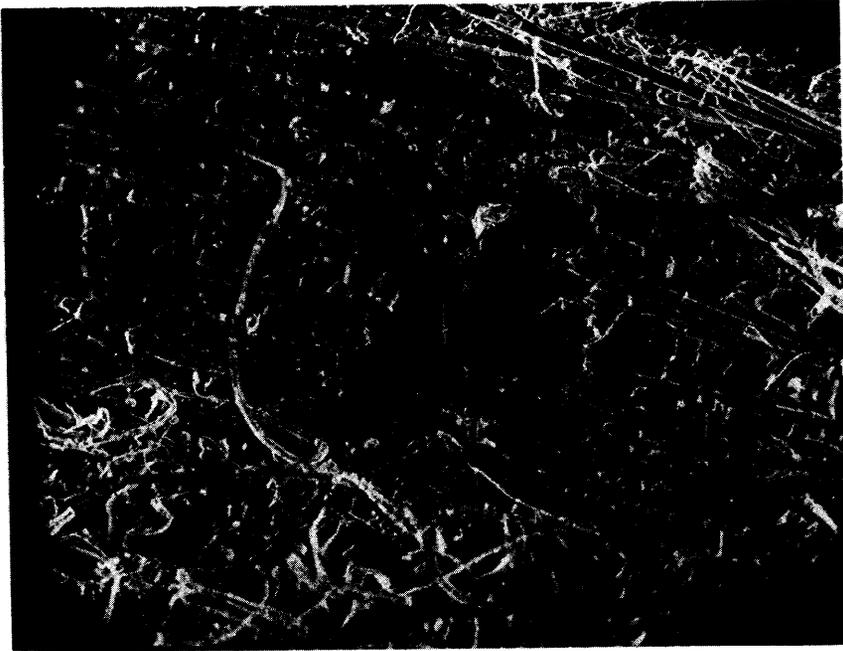
Figure 34b - Fatigue fracture surface in Kevlar/934.

for these data are as follows:

$$S = 6.67 \log N + 375 \quad R = 0.9$$

The environment used during testing of the dry fibers was the same as for the dry laminates. The specimen was enclosed in a polyethylene bag over desiccant as shown in
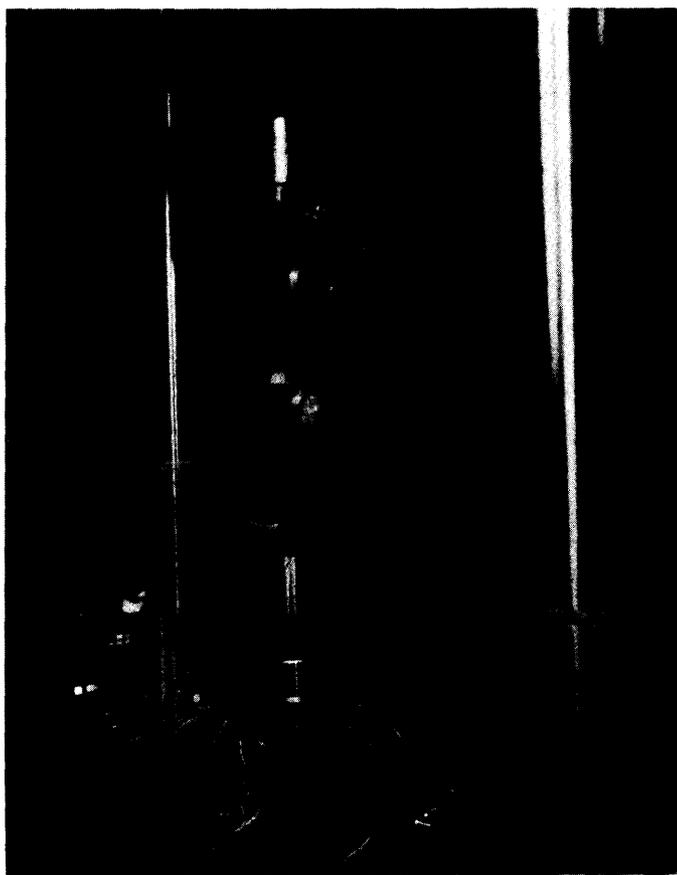
Figure 36 - Instron 1331 testing machine with bagged Kevlar specimen.

Figure 36.
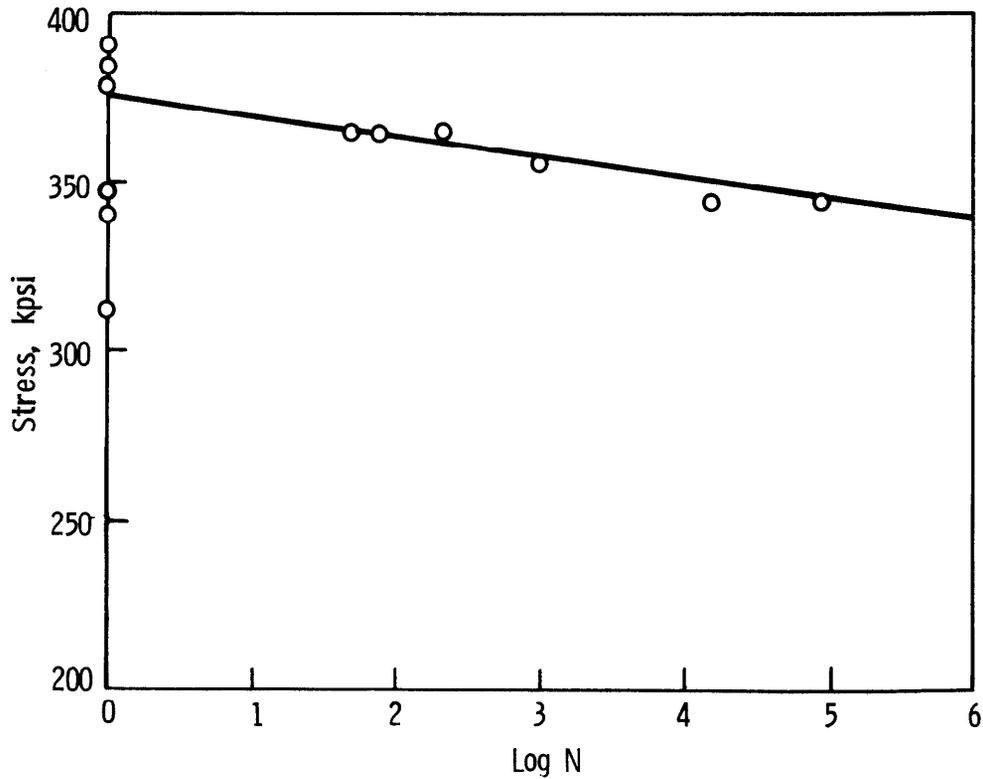
Figure 35 - Tensile fatigue lifetimes for dry Kevlar yarn.

S-log N curve of the dry 195 denier Kevlar fiber. The
Instron 1331 servohydraulic test system was used for these
fatigue tests. The same conditions, R=0.1 and F=10Hz, that
were used for laminate testing were employed for fiber test-
ing also. The dry fibers were conditioned as for tensile
testing. The specimen was the 1" gage tabbed yarn shown in
Figure 25, used also for the tensile tests discussed in sec-
tion V.A.2.

The results of these single-cycle tests are also shown
in Figure 35. The coefficients from the linear regression

The axial cracking results from the stresses which develop during cooldown. The curing stresses vary in a complicated manner throughout the laminate due to factors which include local fiber packing, fiber and void volume fraction, and microfracture. The difference in coefficient of thermal expansion of the fiber and the epoxy is largely responsible for the development of these stresses. The coefficient of the TGMDA-DDS epoxy is $50-60 \times 10^{-6}/C$ in the range from the cure temperature (177C) to room temperature (20,37). A Kevlar fiber has a radial coefficient of $60 \times 10^{-6}/C$ and an axial coefficient of $-2 \times 10^{-6}/C$. The anisotropic thermal expansion of the fiber contributes to the complexitity of the curing stresses. Since the transverse strength of the laminate is only approximately 1000 psi, the failures which are caused by curing stresses occur along the fiber axis. The very slow cooling rate suppresses axial cracking by allowing stress relaxation to relieve the curing stresses as they build up.

B. Interactions of Laminates with Absorbed Moisture.

The dynamic mechanical and thermogravimetric measurements have been used to explore the interactions of the material with moisture. The 934 resin interacts strongly with absorbed moisture. A depression of the glass transition temperature of $50-60°C$ is far in excess of that predicted by the simplified Kelly-Bueche equation for glass transition of an epoxy/water system:

VI. DISCUSSION

The effects of moisture have been studied on the dynamic mechanical properties of the composite and its constituents, and on various mechanical properties of these materials. The fatigue resistance of the composite and of the fiber have been investigated. Answers to some of the questions which were raised at the outset of this study can now be proposed as a result.

A. Characterization Data.

The chemical and physical characterizations of these materials were performed to assure the continuity between this and future work. However, there are certain conclusions which arise from these data which are germane to a discussion of the environmental stability of the composite. One is the fact that this material is undercured. There are 26-27% unreacted epoxide groups in the material as cured, and these represent possible sites for further chemical reaction during environmental exposure. In addition, the in-process cure monitoring of the laminates by acoustic emission indicates that the material has a tendency to develop axial cracking between 150 and 100°C during cooldown. This tendency can be suppressed by using very slow cooling rates, but the material which does not crack may be supporting fairly high residual curing stresses which could affect its interactions with environmental moisture.

swelling coefficients could relieve any stresses built up
during cooldown from the cure temperature.

The radial swelling coefficient of Kevlar fibers has not
been measured directly, but it is probably quite high, since
the equilibrium moisture content is high and the axial
swelling is very small. Estimates as high as 0.73%/% have
been suggested (20). Although this swelling would cause
transverse stresses in the laminate, it might also effec-
tively enhance the fiber/matrix bonding by making the fiber
harder to pull out of the matrix. High radial compressive
stresses in the fiber might also suppress axial splitting of
the fiber, a prevalent failure mode in the fibers, alone and
in the composite.

C. Effects of Moisture on Quasistatic Properties of Lami-
nates.

There is a clearcut increase in the quasi-static tensile
strength of this material upon absorption of moisture. This
effect is observed in the adhesive tab specimen, in the
streamline specimen and in the extrapolation of the fatigue
data to single cycle strength. In all these cases the dif-
ference is 20-30 kpsi, which represents a significant
increase in the strength.

The streamline specimens were tested in order to inves-
tigate the possibility that the difference between wet and
dry strengths could be due to stress concentrations at the
grips which perhaps were affected by moisture absorption.

$$Tg = Vp*Tgp + (1-Vp)*Tgd$$

where Vp is the volume fraction of polymer, Tgp is the glass transition temperature of the polymer, and Tgd is the glass transition temperature of the diluent. This assumes that the coefficients of expansion of the water and of the epoxy are approximately equal. Given Tgd = -90 to -136°C and Tgp = 205°C, the Tg of a fully cured saturated epoxy/water system containing 5% water would be 185-190°C. The measured Tg of 150°C is clearly lower than predicted, and the depression of Tg in this epoxy is larger than that which occurs in many epoxy/water systems.

TGA measurements indicate that the absorbed moisture is strongly bound to the resin. Differences in weight due to retention of absorbed moisture persist up to the onset of thermal degradation in both resin and composite. The pure fibers appear to give up absorbed moisture more readily, but the higher surface to volume ratio of fibers may be responsible for the difference.

The absorption of moisture will change the state of residual stress in the laminate. As moisture is absorbed into the Kevlar/epoxy composite, the resin will swell isotropically, while the fiber swells only slightly in the axial direction. The swelling coefficient for the TGMDA-DDS epoxy is reported to be 0.27% strain/% moisture uptake, while the axial swelling coefficient of the Kevlar is much smaller, perhaps 0.06-0.09%/% moisture (20). This difference in
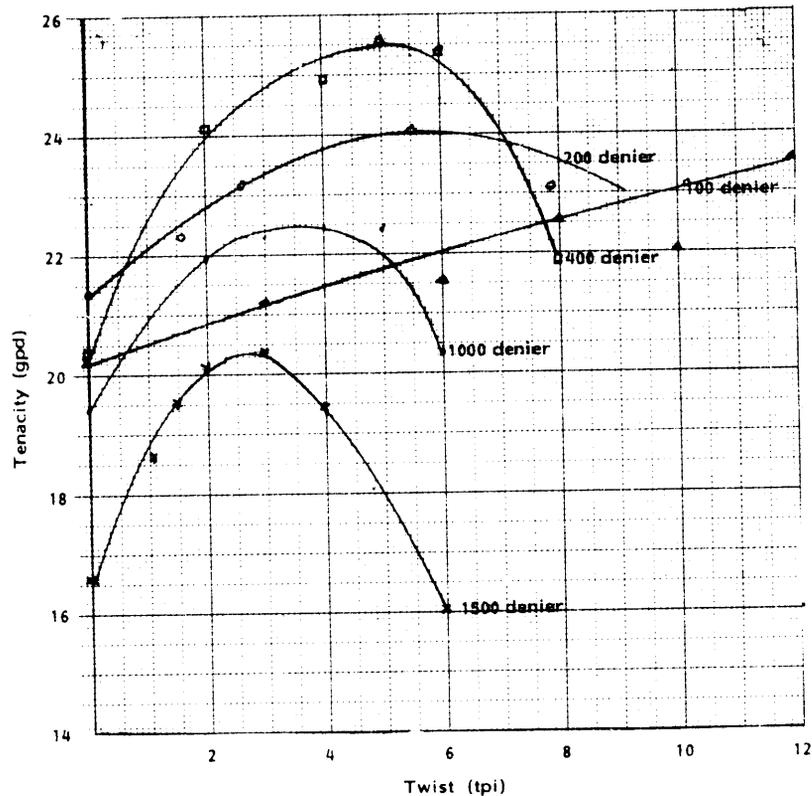
Figure 37 - Effect of twist and denier on strength
of Kevlar yarns (38).

that it is a 3-ply yarn with perhaps one-half to one twist per inch to hold the structure together. Since the plying operation degrades the strength somewhat, the lower values of strength of the 1500 denier yarn are a good estimate for the strength of the Kevlar fibers in the prepreg. As Figure 37 shows, the minimum values would be 16-18 grams/denier, or 290-330 kpsi. At 70% fiber volume fraction, this corresponds to 205-230 kpsi composite strength. All the values obtained for strength of the wet composite are in this

The fact that the measured strength, both wet and dry, is markedly increased and the coefficient of variation is decreased by the use of streamline specimens supports the existence of stress concentrations which affect the measured properties in the straight specimens. The increase in strength in the wet material is still observed, however. This indicates that this increase is independent of specimen geometry, and truly reflects a difference in material properties. The conclusion is supported by a consideration of the strength which would be expected in this composite. Given a Kevlar fiber volume fraction of 70% and a reported fiber strength of 26 grams per denier or approximately 475 kpsi, 230 kpsi is clearly too low for the composite strength; 330 kpsi would be a more likely value. Literature data indicate, however, that a strength of 475 kpsi is the maximum which is attainable under any circumstances, and the strength of the Kevlar fibers in these lamainates is probably lower. Figure 37 is taken from an Air Force Materials Laboratory report (38) on the design of Kevlar parachute material performed by the Fabric Research Laboratories. It shows the strength of Kevlar yarns as a function of denier and twist. The reported strength of 26 grams/denier is seen to be the highest value obtained under any conditions. As the denier increases and the volume of fiber spun per unit time increases, the strength decreases. The 1500 denier yarn is the heaviest denier available. Examination of the 4560 denier yarn used to fabricate the 934 prepreg indicates

explanation has been advanced by these investigators, but Morgan and Sendickyj suggest that it is due to nonlinearity in the stress-strain curves of the fibers themselves, while Zweben and Lifshitz ascribe it to realignment or straightening out of the fibers under load, and a resulting stiffening of the laminate. Zweben believes that the fiber curvature which is observed in both prepreg and fabricated specimens is responsible for this effect. Although a similar fiber curvature is generally observed in graphite/epoxy prepreg, Lifshitz proposes that the fibers are slightly warped in the cured specimen, since they are not under constant tension during cure of the laminate. As a result some fibers are not fully active as load carrying elements until they are stretched and become straight. Lifshitz also reports a 10% increase in the strength of wet specimens, and he proposes an increase in resin ductility which enables the wet material to redistribute stresses more advantageously in the region of local fiber fracture. If the nonlinearity in the composite behavior is due solely to fiber nonlineaarity as Sendeckyj and Morgan suggest, then it should be apparent in the stress-strain behavior of the yarns. As reported in section V, the modulus both of wet and dry tabbed yarn specimens was linear to failure, and absorption of moisture did not change the breaking strength of the yarn. Therefore, our data indicate that the stress-strain behavior of the composite, including fracture, is influenced by the presence of the matrix, and the increase in tensile strength in the

range, and the value of 230 kpsi obtained using the stream-line specimens is probably close to the true strength of the composite. Therefore the strength of the dry specimens is lower by 10% than that which can be obtained with this composite. The failure strain in the wet composites, as shown in Table II and Figure 22, also is approximately 10% higher than that of the dry. This is closer to the failure strain which is observed in unimpregnated Kevlar fibers at this gage length and denier (23). This suggests that the fibers are failing prematurely in the dry composite.

As mentioned in section V, the failure modes are different in the wet and dry material. Tensile failure in the dry specimens is accompanied by one or two major axial splits, whereas the wet specimens undergo much more uniform and extensive splitting at failure. This also suggests a premature failure in the dry material, due to local nonuniformity of stresses in the specimen. The absorption of moisture apparently engenders a more uniform stress at failure, accompanied by higher failure strains. An examination of the stress-strain behavior of the composite, fiber and resin indicates a mechanism by which this may occur. The stress-strain curves both of wet and dry composites, shown in Figure 22, exhibit an upward curvature which is reflected in the E_f values in Table II which are higher than E_i. This effect has been noted in Kevlar/epoxy composites by Zweben (39) and Morgan (24), and in graphite/epoxy composites by Lifshitz (40) and Sendeckyj et al. (41). No conclusive

series of tests, with variations in the loading and unload-
ing sequence. Typical results are shown in Figure 38 and in
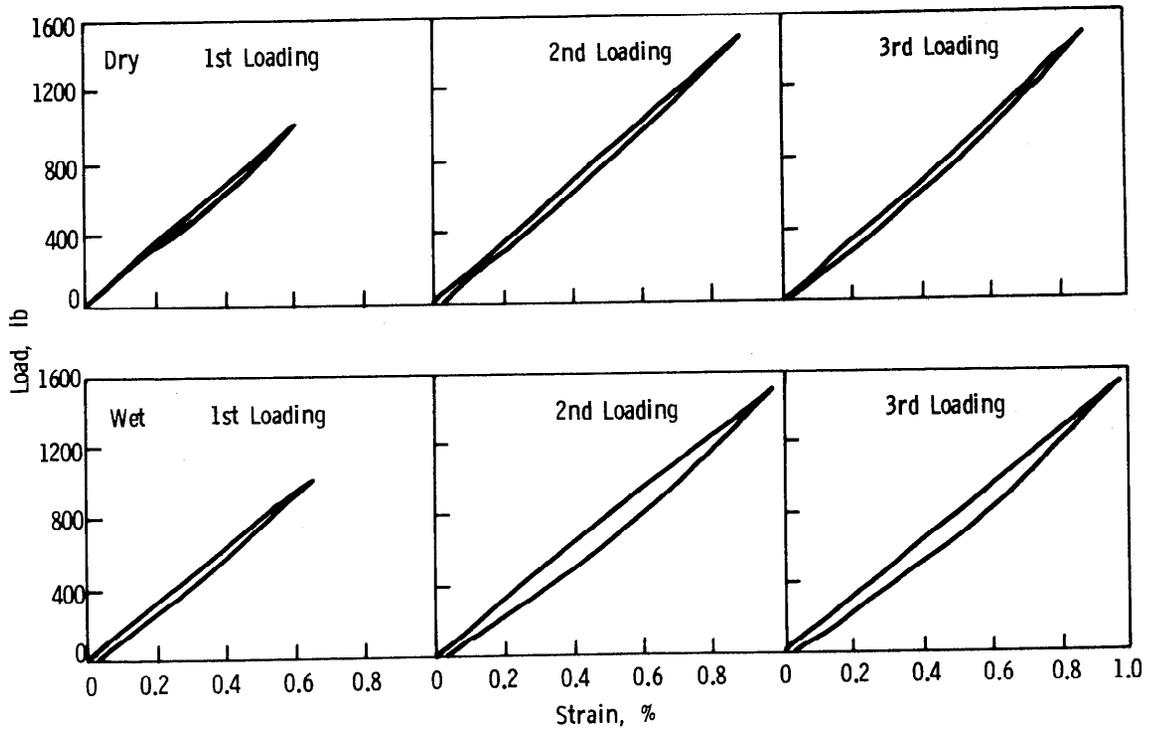
Figure 38 - Effect of moisture on loading/unloading
stress-strain curves in Kevlar/934 laminates.

wet material is due to changes in the matrix properties induced by moisture absorption. Lifshitz performed his study on T-300 graphite fibers in a Narmco 5208 matrix. Since 5208 is also a TGMDA-DDS epoxy, his suggestion that enhanced matrix ductility is responsible for the increased tensile strength in his laminates would also apply to the Kevlar/epoxy. Similar results have been reported by Lauraitis and Sandorff (42) on graphite composites with 5208 and Hercules 3501, another TGMDA-DDS epoxy. We do not observe ductility in the common sense of the word - high strain to fail- in tensile tests of this epoxy, wet or dry. In both cases, brittle tensile fracture occurs before yield or flow. In compression, however, an increase of 15% in f is observed in the wet epoxy. Also, a significant decrease is observed in yield stress with moisture absorption, as shown in Figure 26. Although the initial moduli are similar, the yield stress of the wet epoxy is almost 50% lower than that of the dry. This enhanced deformability of the wet material is an indication of the strong interaction which occurs between this epoxy and water, an interaction which is also reflected by the 50°C depression of Tg by the absorbed moisture.

To investigate the specific mechanism by which this enhanced matrix deformability might affect the stress-strain behavior of the laminates, we performed a series of loading and unloading experiments on wet and dry laminates. Three wet and three dry laminate specimens were tested in these

range below 1000 pounds load, then gradually increases again to failure. This behavior resembles a yielding phenomenon, and is accompanied by an irreversible strain which is 100% greater than that which occurs in the dry composite at the same load. Upon subsequent reloading, the modulus of the wet material appears to be linear up to the previous load, and then begins to increase. The modulus of the dry material is not so strongly affected by previous loading and remains concave upward upon reloading. Although the stress-strain behavior of the dry material is not changed by previous loading, the acoustic emission in the dry specimens indicates that considerably more microfracture is occuring under load than in the wet specimens. These data support the theory that fiber realignment is occuring in these materials under load. Further, they indicate that this realignment is accomplished in the wet material in part by local yielding and deformation of the matrix, and it is more permanent than in the dry material. In the dry material the realignment is largely reversible and occurs by local microfractures of the matrix, the fiber or both. Apparently the deformability of the wet matrix allows the fiber realignment to occur with less damage to fiber and matrix, thereby enabling the composite specimen to fail at a higher and more uniform stress level. This effect is dependent on the strong interaction of this TGMDA-DDS epoxy with moisture, and it may not occur with other Kevlar/epoxy laminates. As evidenced by the work of Lifshitz and the other

Table XI.

TABLE XI.

BEHAVIOR OF KEVLAR/934 LAMINATES
DURING LOADING AND UNLOADING

Loading	DRY irr,%	counts	WET irr,%	counts
1, to 1000 lbs	0.02	426	0.04	185
2, to 1500	0.025	3,225	0.05	956
3, to 1500	0.02	1,000	0.05	165
4, to 2000	0.02	4,484	0.07	4,135
5, to 2000	0.03	1,000	0.06	660
6, to 3000	failed	20,419	0.08	18,910
7, to 3000			0.06	4,944
8, to 3000			0.07	3.500
9, to 3850			failed	27,000

Acoustic emission monitoring was employed during these measurements to detect evidence of microfracture. Table XI lists the number of acoustic emission counts and the irreversible strain which occurred during each cycle of loading. Figure 38 shows the stress-strain behavior of the laminates during the first three cycles of loading.

As was observed in the normal tensile tests of these materials, (Figure 22) although the stress-strain curves of both wet and dry materials are concave upward, the modulus of the wet material first increases then decreases in the

filament-wound structures. There are no data available on filament wound TGMDA-DDS epoxy specimens, however, since its high viscosity makes it an undesirable filament winding resin. Testing of filament wound Kevlar specimens using this resin or strands impregnated with this resin and then cured under fairly high constant tension would be a valuable extension of this current work.

The behavior of the wet and dry materials in the notched tensile tests reflects deformability in the wet composites, and indicates the absence of high residual stresses in the resin. In Figure 27 it can be seen that the load required to initiate and propagate a delamination in the dry material is higher than in the wet material. If the dry material were bearing high stresses in the matrix or at the fiber/matrix interface, the load required to initiate and propagate a delamination should be significantly lower. Figure 27 also shows that the wet composite exhibits greater nonlinearity in load-deflection behavior before the delamination initiates at Li. This is further evidence of the ductility of the resin in the wet composite.

D. Fatigue Resistance of Laminates.

Despite the increase in quasi-static tensile strength in the wet composite, the dry and wet materials lose the same percentage of strength per decade of cycles of tensile loading. This can be shown by dividing the slope of the S-N curve in kpsi/decade by the extrapolation of the stress to

investigators in this field, however, this is an epoxy system which is widely used in the aircraft industry and these results have some general applicability.

To distinguish between the two suggested sources of fiber misalignment in this material, we cured several single ply tensile specimens from sections of the prepreg which were free of apparent curvature or waviness of the type discussed by Zweben. These were cured according to the recommended cure cycle with ends constrained but not under constant tension, and therefore would experience fiber warping of the type suggested by Lifshitz. When these specimens were tested in tension, the stress-strain curves both of the wet and dry materials were concave upward. The wet material failed at approximately 15% higher stress with uniform axial splitting and a failure strain of more than 2%, while the dry material failed with localized splitting at approximately 1.5% strain. The apparent yield region in the wet material was absent in these specimens, however.

Apparently the gross visible fiber misalignment in the prepreg is not responsible for all the phenomena which we observed. Lifshitz's suggestion of fiber warping during cure, perhaps due to the negative coefficient of thermal expansion in graphite and Kevlar fibers, is a valid one. All the studies which have shown an increase in composite strength with increasing moisture have been performed on specimens fabricated from prepreg, and the extent and effects of fiber misalignment may be different in

crack surfaces against each other during loading. Due to
the tendency of fatigue generated cracks to run through the
Kevlar fibers as shown in Figure 34a, such cracks expose the
interior surfaces of the fiber to fatigue damage. The rub-
bing of these internal fracture surfaces during cyclic load-
ing would be expected to generate frictional heating in the
composite when tested at 10 Hz. As shown in Figure 30, this
is the case. Since this heating is much greater in zero
degree plies than in ninety degree plies, the rubbing of the
axial fracture surfaces apparently makes a greater contrib-
ution to the heat generation than does their initiation and
propagation.

To eliminate the possibility that the elevated tempera-
tures which the specimen experiences during fatigue loading
affect the measured fatigue lifetime, we tested four uncon-
ditioned specimens at 160 kpsi maximum stress and 4.5 Hz,
which is the minimum frequency of the Instron 1211 cycler.
We found that the temperatures throughout the lifetime were
20-25 C lower, with a stable temperature of approximately
40 C throughout most of the test in all cases. Despite the
difference in specimen temperature, the fatigue lifetimes of
these specimens were similar to those of the specimens at 10
Hz. The mean log lifetime for the four unconditioned speci-
mens was 5.01, which is between the values of 4.63 and 5.06
for the dry and wet material respectively. The lack of
dependence of fatigue lifetime on specimen temperature in
this range is also supported by the linearity of the S-log N

single-cycle strength. Although the slopes of the S-N curves for the wet and dry materials are -15.56 and -13.80 respectively, normalized by the single-cycle strength they become 6.5% and 6.2% per decade. This indicates that the mechanism of failure which controls the behavior in fatigue is the same in both the wet and dry material.

The S-N curves may flatten out in the high stress, short time region, although the Instron 1211 cycler has startup times which preclude careful measurements in this range. During this time the fatigue loads are built up gradually and this could give rise to some flattening of the S-N curve. After the initial 100 cycles of loading, the S-N curves are fairly linear, although there is more scatter in the dry material than in the wet. These data imply a single controlling mechanism of fatigue failure in the range from 10 to 10 cycles, which is the same for wet and dry materials, although the wet material exhibits a longer lifetime at all stress levels throughout the range of 130 to 200 kpsi due to its higher initial strength.

Examination of the damage which is observed in the materials during fatigue loading and failure is helpful in postulating a mechanism of fatigue failure in these materials. As shown in Figure 34c, the tendency of the fiber to split and fibrilate is evident in the fatigue failure of the laminate. The surface shown in Figure 34b is a fatigue fracture surface, apparertly initiating from a void or a flaw. It is quite rough in appearance, probably from rubbing of the two
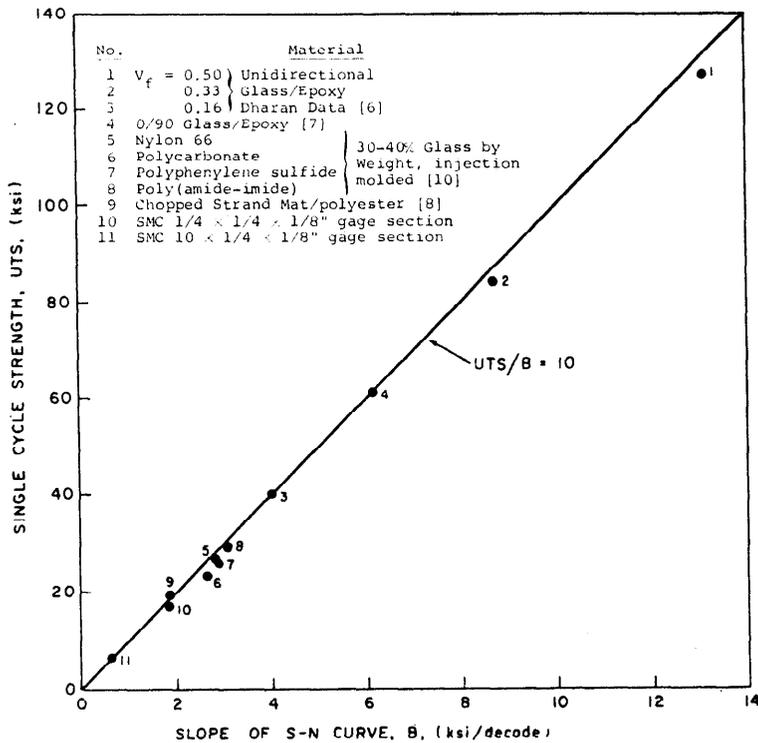
Figure 39 - Correlation between tensile strength and fatigue failure in glass composites (from J. Mandell).

Kevlar/epoxy composites as in glass reinforced materials, it is a possible mechanism of fatigue failure in the Kevlar/934 laminates.

Our work on Kevlar yarns, which is in agreement with other published data (44) (see Figure 40), indicates a much more gradual slope of the yarn S-N curve - 1.7% loss of strength per decade - than the laminate curve. Apparently, fiber-fiber abrasion is not controlling the fatigue failure in the composite, since the data for fiber and composite

curve. Since specimen temperatures vary as much as 50 C through the range of maximum stress from 130 to 180 kpsi, a dependence on temperature would be expected to cause some change of the slope of the S-log N curves in this range. This is not the case.

Although the specimen temperature does not appear to affect the lifetime, Figure 33 shows there is a correlation between T_i, the initial heating rate, and the ultimate life-time. This suggests that the controlling mechanism of fatigue failure is one which makes a dominant contribution to the heat generation. Since the rubbing of the surfaces of internal fatigue cracks is responsible for a large part of this heat generation, the damage to these surfaces caused by rubbing or abrasion is a likely candidate for the mechanism of fatigue failure.

It is instructive at this point to compare these data to the tension-tension fatigue behavior of glass/epoxy composites. The loss of approximately 6% of ultimate tensile strength per decade of loading compares favorably with that of glass. In a surprising variety of glass composites, both with thermoset and thermoplastic matrices, the strength loss is 10% per decade (43) (see Figure 39). Glass yarns tested in tension-tension fatigue also lose 10% of UTS per decade. This indicates that the mechanism which dominates yarn fatigue - probably fiber-fiber abrasion - is also control-ling the fatigue in the composite. Since fiber-fiber abrasion would generate heat, and could occur as easily in
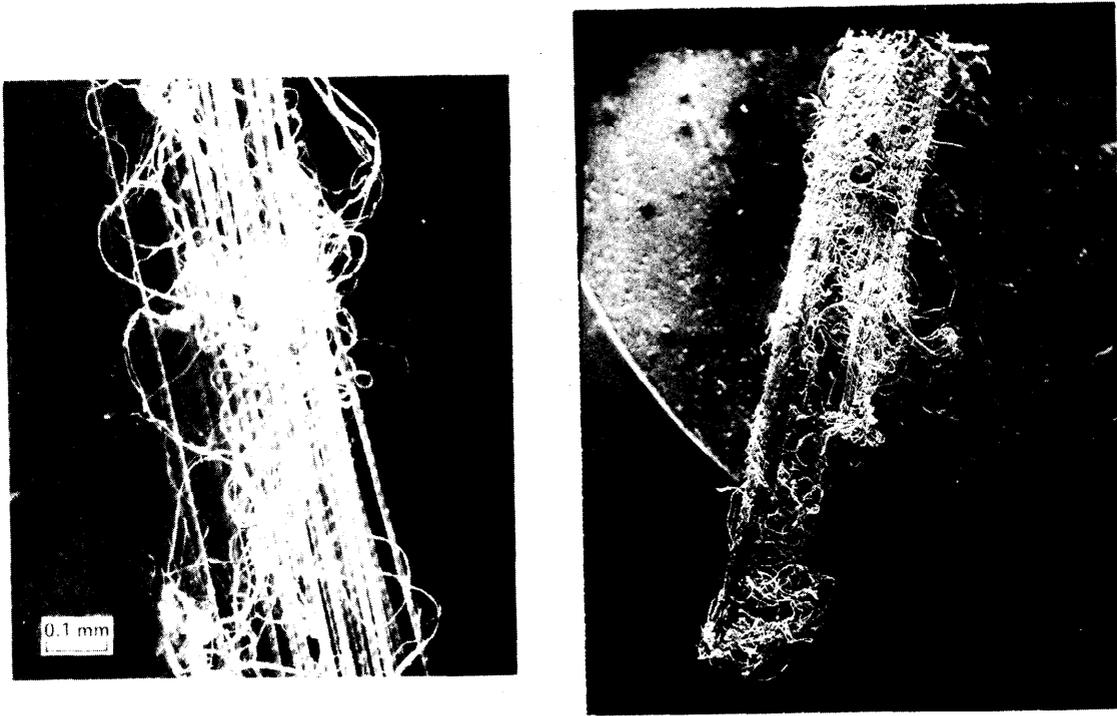
Figure 41 - Comparison of abrasion damage in Kevlar Yarns
(left) and fatigue failure of Kevlar/934 composite (right).
(Micrograph on left from reference 45).

fiber damage which occurs both to the outside and interior
of Kevlar fibers during fatigue failure.   These micrographs
are evidence that abrasion damage is occurring to the Kevlar
during fatigue failure.   Further evidence that abrasion dam-
age of the fibers is the mechanism of fatigue failure in the
laminates is shown in Figure 43.   These are data replotted
from part I of the Kevlar abrasion study cited above (46).
They show a linear relationship between loss of tensile
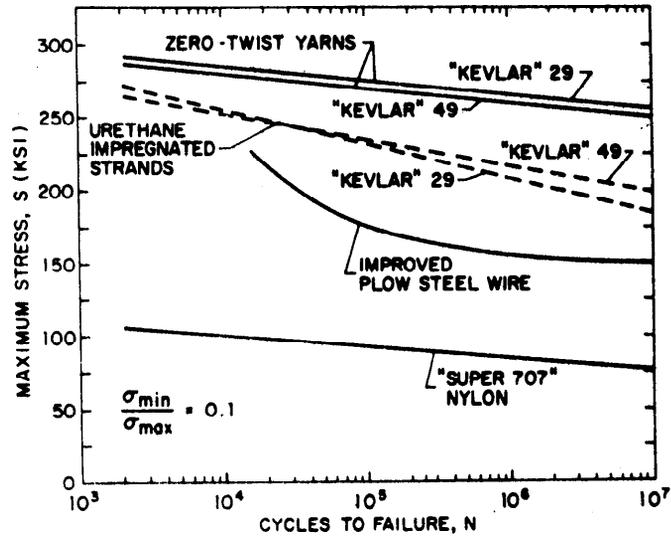
Figure 40 - Fatigue response of Kevlar yarn (42).

would be similar if that were the case. Yet some form of
abrasion is indicated by the heat generation data. Further
evidence for the occurrence of abrasion during fatigue load-
ing in these laminates is found in Figures 41 and 42, which
compare the behavior of the material in tension, fatigue and
abrasion. Figure 41 shows a fatigue fracture in a Kev-
lar/934 specimen on the left compared to a bundle of Kevlar
fibers which have been subject to abrasion against a metal
rod (45). The large amount of fiber damage in both cases is
characteristic of abrasion. This failure is quite different
from tensile failure of a Kevlar filament, shown at the left
of Figure 42. This is compared with a micrograph at the
right at comparable magnification showing the extensive
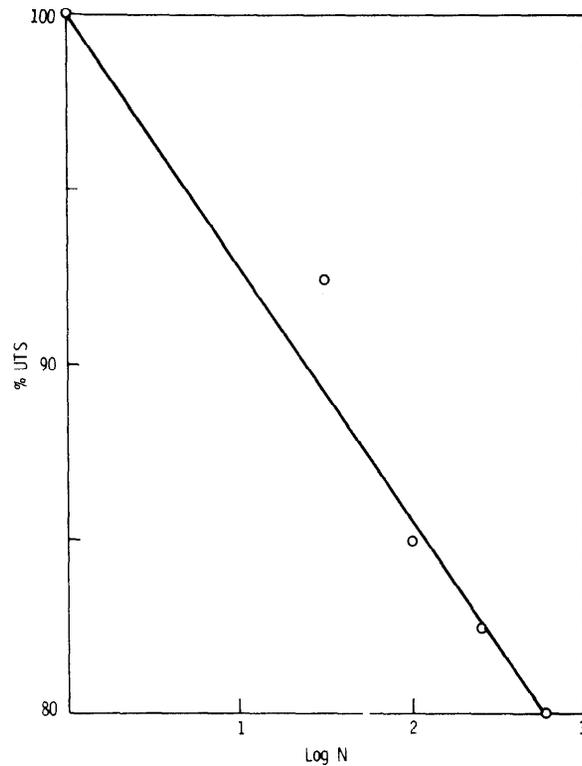
Figure 43 - Percent of ultimate tensile strength retained by
Kevlar yarns after abrasion under tensile load.
(Data replotted from reference 46.)

and their fatigue behavior is significantly different than
the laminates. The data in Figure 40 suggest that, as in
the case of quasi-static stress-strain behavior, the pres-
ence of the matrix markedly alters the fatigue behavior of
the Kevlar fibers. The fatigue behavior of dry Kevlar yarns
in Figure 40 is in agreement with our yarn data, but the
behavior of impregnated yarns in Figure 40 is different, and
in fact is the same as that of our composite specimens.
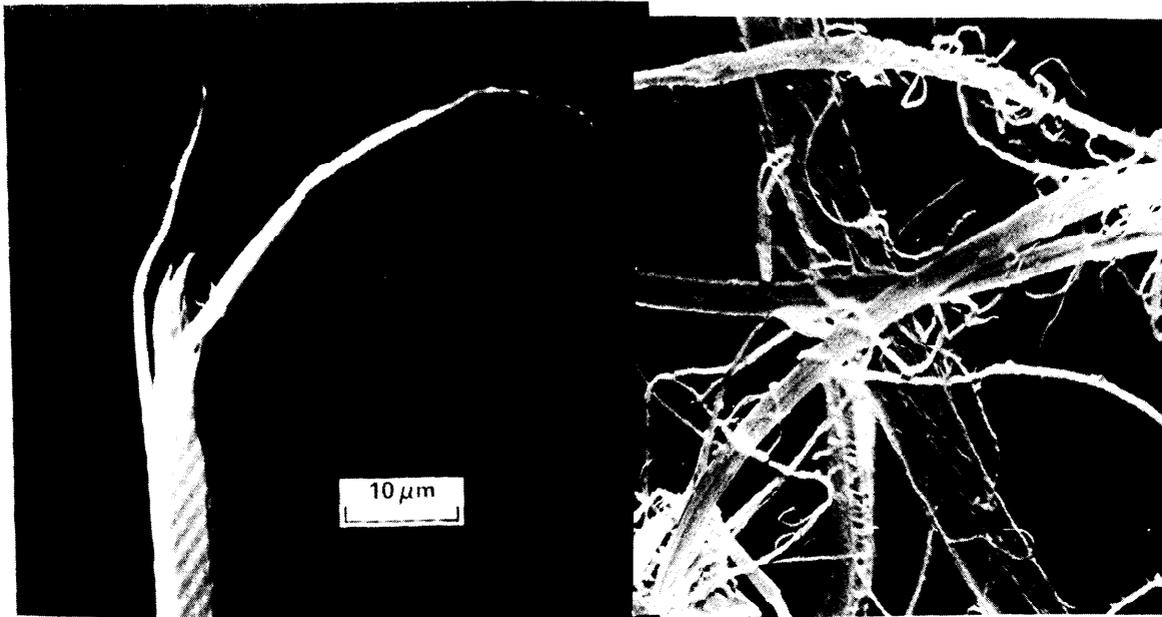
Figure 42 - Comparison of tensile failure

of a Kevlar filament (left) and failure of Kevlar filaments

in Kevlar/934 composite under

tensile fatigue loading (right).

(Micrograph on left from reference 45.)

strength and log cycles of abrasion, with a 6-7% loss of strength per decade of cycles of abrasion.

Similarities in damage modes and strength loss between abraded Kevlar yarns and these Kevlar/epoxy fatigue specimens suggest that some type of fiber abrasion is the mechanism of fatigue failure in the composite, although they do not constitute proof. If fiber abrasion does control the composite fatigue behavior, it cannot be simple fiber-fiber abrasion, since this must occur in the dry yarn specimens,

reported here.   Therefore, it is likely that the similarity between rate of strength loss of Kevlar/epoxy composites in static and cyclic fatigue is coincidental, and the mechanism of static fatigue failure in these materials is probably different from that which occurs under cyclic loading.

Both impregnated strands and Kevlar/934 laminates lose 6-7% of UTS per decade of fatigue loading. The fiber abrasion which occurs during fatigue loading of composites and impregnated strands could be abrasion of the fiber by the surface of the matrix at the fiber-matrix interface. It could also be abrasion of the fiber internally, since in the presence of a matrix, tensile loading tends to cause intrafiber failures rather than failure at the fiber-matrix interface. This is due to the low transverse strength of the fiber. Similar intrafiber abrasion could occur during abrasion of a Kevlar yarn over the curved surface of a smooth metal rod.

There are some similarities between the cyclic fatigue behavior of these laminates and the reported stress-rupture or static fatigue behavior of Kevlar/epoxy strands and pressure vessels (47). In both cases there is no well-defined fatigue limit, and the rate of strength loss is 6-7% of ultimate tensile strength per decade of time. Under static fatigue, however, the lifetimes are five orders of magnitude longer. Although there has been no discussion in the literature of the mechanism of stress rupture in these materials, there is apparently a decrease in the axial split lengths in Kevlar fibers which experience stress rupture at long times (24). This suggests that some morphological or chemical changes may be occurring in the fibers after long times under load. Such changes would probably not occur in the fibers during the relatively short term cyclic fatigue tests

material by its longer lifetimes throughout the range of stresses which we have investigated. The rate of strength loss in tension-tension fatigue of 6-7% of ultimate tensile strength per decade does not depend upon moisture content, however. This indicates that the matrix deformability which increases the ultimate tensile strength does not change the mechanism of failure of the material in fatigue.

The marked heat buildup which occurs in these materials during fatigue loading can be correlated with specimen lifetime, indicating that the controlling mechanism of fatigue failure is one which makes a dominant contribution to heat generation. Examination of failure modes, and comparison with studies of abrasion resistance of Kevlar yarns, suggest that the mechanism of tension-tension fatigue failure in these laminates depends upon the presence of the matrix and is probably degradation of fiber strength due to fiber/matrix or intrafiber abrasion.

There are a number of areas of future research which appear promising. A thorough investigation of the complicated moisture uptake behavior of this material is now underway. In addition to careful and frequent weight measurements of immersion specimens at various temperatures, this investigation includes finite-element analysis of the diffusion as a function of various parameters such as fiber volume fraction and local fiber arrangements. The approach of this finite element study has been to model a single circular fiber or array of fibers surrounded by a matrix

VII. CONCLUSIONS AND RECOMMENDATIONS.

The major conclusion which can be drawn from this study is as follows: Moisture absorption affects the properties of this Kevlar/epoxy composite primarily by interaction with the TGMDA-DDS epoxy which it employs. The absorption of 5% weight of water lowers the glass transition temperature of the cured resin by 50-60°C, significantly reducing the high temperature stability of the wet laminates. Absorbed water may also react chemically with the 27-30% unconverted epoxide still present in the matrix of the cured laminate, complicating the moisture uptake, which is non-Fickian. Absorption of moisture also decreases the yield stress of the cured epoxy measured in compression by almost 50%. This increase in matrix deformability allows local fiber realignment under load in the wet composite to occur with less damage to fiber and matrix. This allows the wet composite to fail at a higher strain and at a higher and more uniform stress level. Also, it is reflected in a higher level of irreversible strain in the wet material and a more nearly linear stress-strain curve upon reloading. The misalignment of fibers in the composite is probably a form of warping which occurs during cure. The realignment of these fibers under load causes the modulus both of wet and dry composites to increase with increasing load.

The fatigue behavior of the wet and dry material reflects the 10% higher single-cycle strength of the wet

The results of this study suggest that the use of more ductile epoxies in Kevlar composites might result in improved mechanical properties. The so-called flexible epoxies which have been found to improve the burst strength of Kevlar epoxy filament wound pressure vessels are one possibility. Rubber toughened epoxies are another. They might achieve enhanced toughness without sacrificing high temperature stability. The flexible epoxies are cured at relatively low temperature, which rules out high temperature stability, but their use would alleviate fabrication difficulties due to curing stresses. They might also lessen the extent of fiber/matrix abrasion which seems to dominate the fatigue behavior in this material.

For future studies of fatigue behavior in this or any material, the streamline specimen configuration is strongly recommended. Although some care is required to prevent slipping in the grips (use of adhesive tabs is one effective means of preventing slippage), the failures obtained with this specimen were good. A unidirectional Kevlar/epoxy laminate has a very high ratio of tensile strength to shear strength, and it is difficult to obtain valid tensile strength data on such a material. Since good results were obtained in this study with the streamline configuration, it should be possible to obtain valid strength and fatigue data on many other composite materials using this specimen design.

material with a different diffusion coefficient. Predicted diffusion behavior of these models is being correlated with experimental measurements on Kevlar/934 laminates. FTIR measurements also will be employed, to study the disappearance of residual epoxide groups as a function of immersion time.

Our results indicate the potential use of careful thermographic measurements of initial heat buildup during fatigue loading as a technique for prediction of lifetime. The scanning infrared camera described in section V is being used to characterize the thermal response of the entire composite specimen to fatigue loading, as a function of stress level and loading frequency. If the technique can be sufficiently refined, it could be applicable to any material in which heat generation accompanies the dominant mode of fatigue damage. Therefore, it should be useful with the wide range of glass composites which apparently fail in fatigue by fiber-fiber abrasion.

The source of nonlinearity in the stress-strain curve of the laminates should be investigated by studies on impregnated Kevlar strands cured with various levels of yarn tension. Tensile tests as a function of moisture content should be made on these strands to determine the effect of fiber alignment on their tensile strength. Similar tests using another epoxy should also be performed, since other epoxies will not interact so strongly with absorbed moisture.

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APPENDIX

DATA

A. TENSILE STRENGTH AND STIFFNESS OF LAMINATE STRIP SPECIMENS

Data summarized in Table II, page 66

WET LAMINATES

UTS, kpsi	E_i, Mpsi	E_f, Mpsi	ϵ_f, %
212	10.40	13.00	1.70
183	10.90	13.73	1.91
227	10.80	12.43	1.88
242	10.67	12.12	1.75
178	11.21	13.74	1.77
222			
215			
184			
176			
169			
228			
237			
217			
210			

BIOGRAPHICAL NOTE

Margaret Eileen Roylance was born 6 July 1946 in Salt Lake City, Utah. She attended parochial schools there and matriculated at the University of Utah, receiving an Honors Bachelor of Arts degree in 1968. She accepted a position as physicist with the Army Materials and Mechanics Research Center in 1969, and has been employed there since then. She has published a number of journal articles and reports dealing with her research at AMMRC, primarily in the mechanical and environmental properties of polymeric and composite materials. She received a Master of Science degree in Civil Engineering (Materials Program) from MIT in 1973.

She was married to David Roylance in 1968 and has two children, Stephen and Patricia, aged seven and four.

B. STRENGTH OF LAMINATE STREAMLINE SPECIMENS

Summarized in Table III, page 70

LAMINATE UTS, kpsi	WET LAMINATE UTS, kpsi
208	238
211	224
205	210
215	230
209	240
214	240

DRY LAMINATES

UTS, kpsi	Ei, Mpsi	Ef, Mpsi	ɛf, %
164.5	10.60	11.50	1.60
169.2	10.81	11.81	1.60
190.3	9.92	13.98	1.58
173.2	11.50	13.50	1.61
193.1	11.75	13.47	1.61
196.8	12.15	13.75	1.6
194.9			
184.1			
172.2			
191.7			
179.1			
191.1			
171.1			
164.5			
169.2			

UTS of tabbed 195 denier yarns, kpsi.

RATE	DRY	WET
10 Hz*	384	380
	392	372
	379	401
	340	405
	315	350
	348	330
	405	365
	406	355

RATE	DRY	WET
0.005"/min	296	379
	384	394
	340	396
	379	342
	362	388
	383	337
	404	365
	407	360

* Effective frequency of single-cycle test.

C. STRENGTH OF KEVLAR FIBERS

Summarized in Table IV, page 72

UTS of yarn from prepreg, kpsi (unconditioned)

200

189

240

235

179

192

244

154

UTS of capstan 195 denier specimens, kpsi.

DRY	DRY	WET	WET	UNCONDITIONED	
327	290	297	376	314	346
325	226	335	255	314	372
243	205	364	335	325	338
336	279	387	297	368	299
219	214	365	338	334	282
262	308	362	370	267	295
325	308	224	340	342	205
279	290	374	360	316	333
318	292	288	281	278	359
253	286	394	350	282	226

Saturated resin (18 days at 80 deg C)

UTS, kpsi	E, kpsi	ϵf, %
6.22	511	1.3
7.46	533	1.6
6.93	523	1.5
7.82	523	1.7
7.05	516	1.4
6.36	505	1.4
8.21	595	1.8

D. TENSILE STRENGTH AND STIFFNESS OF 934 EPOXY

Summarized in Table V, page 75.

Dry resin

UTS, kpsi	E, kpsi	ϵf, %
9.63	624	1.6
7.75	605	2.0
13.02	585	2.2
12.30	584	2.4
11.22	591	3.4

Wet resin (18 days at 50 deg C)

UTS, kpsi	E, kpsi	ϵf, %
8.50	494	2.2
8.80	498	2.1
858	504	2.5
9.83	5.9	2.5
9.85	501	2.0
8.88	546	2.0

F. FLEXURE STRENGTH AND STIFFNESS OF LAMINATE SPECIMENS

Summarized in Table VII, page 78

DRY LAMINATES		WET LAMINATES	
σf, kpsi	E, Mpsi	σf, kpsi	E, Mpsi
87.5	9.30	84.7	8.72
82.5	8.56	75.8	8.86
82.8	8.85	76.5	8.93
78.7	7.99	77.0	8.95
80.4	8.18	76.9	8.98
82.5	8.04	77.3	7.65
84.3	8.38	77.6	7.46
89.2	9.43	69.5	8.52
88.9	9.55	68.8	8.77
86.9	8.96	75.4	8.04
88.1	9.11	76.7	8.56
89.2	9.25	78.0	8.83
89.4	9.17	82.8	8.54
86.9	8.58	76-0	8.86
87.0	8.64	73.7	6.68
86.2	8.72	77.6	7.23
84.8	8.38	61.0	
		65.0	

E. COMPRESSION STRENGTH AND STIFFNESS
OF 934 EPOXY

Summarized in Table VI, page 76.

DRY RESIN

E_i, kpsi	σ_y, kpsi	ϵ_y, %	σ_f, kpsi	ϵ_f, %
400	28.4	0.128	28.2	0.156
357	30.8	0.122	42.0	0.388
400	30.1	0.128	38.6	0.368
400	29.2	0.122	45.0	0.410
400	28.9	0.110	40.2	0.370
400	29.0	0.124	44.4	0.430

WET RESIN (immersed at 50 deg C for 3 months).

E_i, kpsi	σ_y, kpsi	ϵ_y, %	σ_y, kpsi	ϵ_f, %
359	17.4	0.090	39.3	0.466
371	17.4	0.090	43.6	0.484
365	17.3	0.102	35.6	0.468
367	17.2	0.094	41.4	0.482
369	17.8	0.096	34.7	0.448
343	17.5	0.094	39.8	0.470

G. NOTCHED TENSILE TESTS ON LAMINATE SPECIMENS

Summarized in Table VIII, page 79

WET		DRY	
L_i, lb.	L_f, lb.	L_i, lb.	L_f, lb.
760	1440	800	1280
720	1605	750	1525
720	1540	760	1525
720	1500	760	1470
745	1460	780	1416

UNCONDITIONED LAMINATES

σf, kpsi	E, Mpsi	σf, kpsi	E, Mpsi
82.3	9.20	82.2	8.72
83.7	9.40	81.6	8.81
82.9	9.26	84.5	9.30
82.9	9.17	84.6	9.09
83.6	9.13	81.4	8.61
84.7	9.25	79.2	8.37
75.9	7.98	80.1	8.54
77.0	8.08	80.4	8.63
79.5	8.35	81.3	8.61
80.2	8.47	80.7	8.61
80.1	8.51	83.7	8.99
78.6	8.40	83.4	9.07
81.0	8.60	84.8	9.14
79.8	8.46	84.9	9.33
82.8	9.00	83.3	8.97
84.6	9.13	84.6	9.34
84.6	9.13	78.0	8.73
85.6	9.56	79.1	8.62
83.4	9.06	81.8	8.99
83.5	9.10	83.8	9.23
84.0	9.30	85.5	9.28
84.7	9.39	84.9	9.20
84.4	9.31	84.8	9.25

	5.62
	5.69
	4.77
	5.80
	6.11
140	5.73
	5.75
	5.67
	5.24
	6.04
130	5.51
	5.57
	6.00
	6.00
	6.56

WET LAMINATES

200	2.69
	2.72
	2.68
190	2.66
	2.91
	3.21
180	4.36

H. LAMINATE FATIGUE DATA

Summarized in Table IX, page 83

DRY LAMINATES

Maximum Tensile stress	Log lifetime
180 kpsi	2.76
	2.74
	2.70
	2.68
170	5.09
	2.77
	5.45
	2.18
	2.19
160	5.38
	4.46
	5.90
	3.65
	3.40
	5.66
	4.35
150	5.59
	5.02
	5.65

I. TENSILE STRENGTH OF DRY LAMINATE STRIP SPECIMENS AT VARIOUS DEFORMATION RATES

Rate, inches/min.	UTS, kpsi
0.005	219
	177
	181
0.05	178
	187
	205
0.5	179
	140
	164
5.0	153
	172
	181

	3.82
	3.01
	3.21
170	5.34
	5.31
	4.25
	4.61
	3.63
160	5.07
	5.51
	4.97
	4.69
150	6.82
	5.34
	5.17
140	6.00
	6.29
	6.15
130	6.92
	7.09
	7.05

K. TENSILE STRENGTH AND STIFFNESS
OF ONE-PLY KEVLAR/934 SPECIMENS

	UTS, kpsi	Ei, Mpsi	Ef, Mpsi	ϵf, %
Wet	184.1	9.09	9.69	2.40
Wet	184.7	8.74	9.76	---
Wet	198.0	8.02	11.1	---
Dry	160.2	11.1	12.9	1.40
Dry	165.6	10.2	11.6	1.59
Dry	156.4	9.37	10.3	---

J. LOG LIFETIME AND INITIAL HEATING RATE

OF WET LAMINATE SPECIMENS DURING FATIGUE

Data plotted in Figure 33, page 87

Maximum Stress, kpsi	Log Lifetime	Heating Rate, deg C/min
190	3.95	52
180	3.01	65
180	3.82	57.5
180	4.36	58
170	3.63	67
170	5.31	49
170	5.34	46
160	4.97	52
160	5.07	41
150	4.55	48
150	5.17	33
150	5.34	51
150	6.82	22
140	6.15	35
130	6.68	34

M. FATIGUE LIFETIMES OF UNCONDITIONED KEVLAR/934 LAMINATES

AT 4.5 HERTZ

Maximum tensile Stress, kpsi	Lifetime, cycles
160	57,540
160	77,770
160	88,480
160	126,310

L. KEVLAR YARN FATIGUE DATA

Displayed in Figure 35, page 92.

Max. stress, kpsi	Log lifetime
345	4.18
345	4.88
345	5.05
355	2.99
370	2.35
368	1.65
368	1.95
280	6.21 (runout)

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